



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:

J. Zhang, X.-J. Wu, Z. Wang, Yu Chen, X. Wang, M. Zhou, H. Scheer, K. Zhao*

Single Fused Gene Approach to Photoswitchable and Fluorescent Biliproteins

Y. Sohma,* Q. Hua, J. Whittaker, M. A. Weiss, S. B. H. Kent*
Design and Folding of [GluA4(O^βThrB30)]Insulin (Ester Insulin), a Minimal Proinsulin Surrogate Chemically Convertible into Human Insulin

J. Esteban, J. V. Ros-Lis, R. Martínez-Máñez,* M. D. Marcos, M. Moragues, J. Soto, F. Sancenón

Sensitive and Selective Chromogenic Sensing of Carbon Monoxide by Using Metalated Binuclear Rhodium Complexes

A. C. Stelzer, J. D. Kratz, Qi Zhang, H. M. Al-Hashimi*
RNA Dynamics by Design: Biasing Ensemble towards Ligand-Bound States

T. Ikawa, A. Takagi, Y. Kurita, K. Saito, K. Azechi, M. Egi, K. Kakiguchi, Y. Kita, S. Akai*

Preparation of Borylbenzynes and their use in the Regioselective Diels–Alder Reaction: Synthesis of Functionalized Arylboronates

Z. Zhang, Z. Wang, R. Zhang, K. Ding*
Extremely Efficient Titanium Catalyst for the Enantioselective Cyanation of Aldehydes by Using Cooperative Catalysis

Qi Wang, M. Zhang, C. Chen, W. Ma, J. Zhao*
Photocatalytic Aerobic Oxidation of Alcohols on TiO₂: The Acceleration Effect of Bronsted Acids

Ye Fu, Q. Dai, W. Zhang, J. Ren, T. Pan,* C. He*
AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of 5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA



“My biggest motivation is curiosity.
The secret of being a successful scientist is to constantly raise one’s standards and creativity ...”
This and more about Ivan Huc can be found on page 4704.

Author Profile

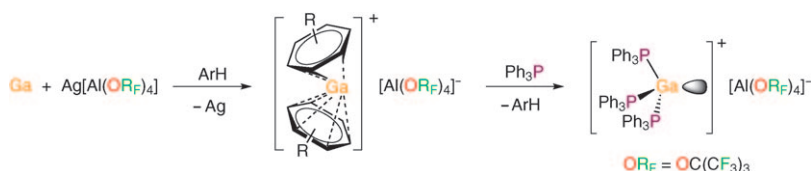
Ivan Huc ————— 4704

Reactive Intermediates

Leonardo S. Santos

Books

reviewed by D. Kuck ————— 4705



The power of one: A stable gallium(I) cation has been prepared by a redox reaction (see scheme) and is stabilized by a weakly coordinating anion. The facile

synthesis of the phosphine cation $[(\text{Ph}_3\text{P})_3\text{Ga}]^+$ is promising for the development of a rich coordination chemistry.

Highlights

Gallium(I) Chemistry

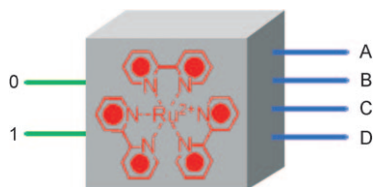
R. J. Wehmschulte* ————— 4708 – 4709

At Last: A Stable Univalent Gallium Cation

Molecular Computers

H. Tian* _____ 4710–4712

Data Processing on a Unimolecular Platform



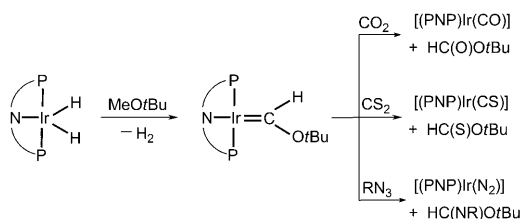
En route to bits and bytes: The integration of complex logic functions within individual molecules allows data processing at the molecular level, as demonstrated by recently reported molecular encoder and decoder devices. This research on decision-making molecules has great potential for future applications and more complex computing on a functional unimolecular platform.

Reviews

C–H Activation

H. Werner* _____ 4714–4728

Carbene–Transition Metal Complexes Formed by Double C–H Bond Activation



Two at one blow: Fischer carbene–transition metal complexes are accessible by double α -C–H bond activation of alkane or cycloalkane derivatives containing an OR or NR₂ functional group. Such complexes with M = Ir react with small mole-

cules, such as CO₂, CS₂, and COS, and with azides (RN₃) and N₂O, by an atom- or group-transfer metathesis, which offers a novel possibility for C–H bond functionalization.

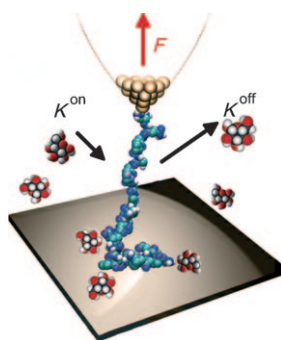
Communications

Single-Molecule Studies

M. Geisler, R. R. Netz,
T. Hugel* _____ 4730–4733



Pulling a Single Polymer Molecule off a Substrate Reveals the Binding Thermodynamics of Cosolutes



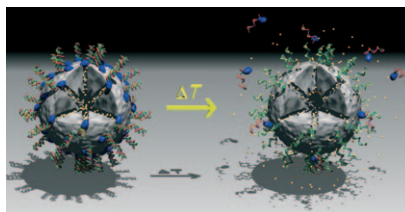
To bind or not to bind: Cosolutes modify, or even determine, the interactions between macromolecules and surfaces. A combination of single-molecule atomic force microscopy with thermodynamic modeling allows the extraction of the binding parameters of cosolutes onto a macromolecule in solution and also in its surface-adsorbed state.

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

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

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

Letting off steam: A temperature-controlled valve system permits the targeted release of guest fluorescein molecules from the pores of colloidal mesoporous silica particles. The pore-opening temperature is dependent on the length of double-stranded DNA linkers. Avidin proteins that are joined to the DNA by a biotin modification act as the molecular valve at the exits to the pores.



Programmable Host–Guest Systems

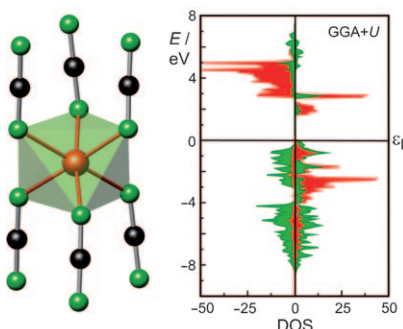


A. Schlossbauer, S. Warncke,
P. M. E. Gramlich, J. Kecht, A. Manetto,
T. Carell, T. Bein* — 4734–4737

A Programmable DNA-Based Molecular
Valve for Colloidal Mesoporous Silica



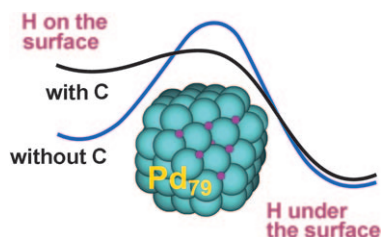
The same, but different: Chromium(III) carbodiimide (see structure), the first ferromagnetic carbodiimide, was synthesized from CrCl_3 and ZnNCN and was characterized by X-ray diffraction. Despite being isostructural with antiferromagnetic Cr_2O_3 , $\text{Cr}_2(\text{NCN})_3$ adopts a ferromagnetic ground state as shown by SQUID measurements and correlated density-functional theory. At low temperatures, the phase shows a slightly larger magnetization than maghemite.



Ferromagnetic Carbodiimide

X. Tang, H. Xiang, X. Liu, M. Speldrich,
R. Dronskowski* — 4738–4742

A Ferromagnetic Carbodiimide:
 $\text{Cr}_2(\text{NCN})_3$



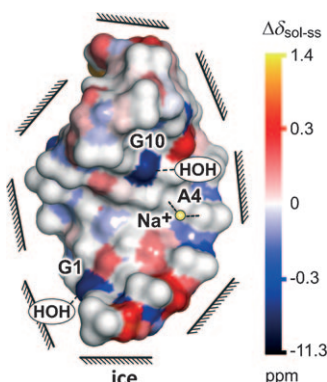
The activation barrier for subsurface migration of surface hydrogen atoms on (111) facets of palladium nanoparticles drastically decreases or even vanishes in the presence of subsurface carbon atoms deposited nearby (see energy diagram). On regular $\text{Pd}(111)$ surfaces, this promoting effect is essentially absent because of the hindered lateral mobility of the surface metal atoms.

Heterogeneous Catalysis

K. M. Neyman,*
S. Schauermaier* — 4743–4746

Hydrogen Diffusion into Palladium
Nanoparticles: Pivotal Promotion by
Carbon

Chilling out: Solid-state ^{13}C NMR correlation spectroscopy was used to assign the signals of a uniformly labeled RNA hairpin in frozen aqueous solution. Conformational analysis shows that solutions of biologically relevant RNAs can freeze without significant changes in RNA structure and without critical loss of resolution and sensitivity in NMR experiments.



NMR Studies of RNA

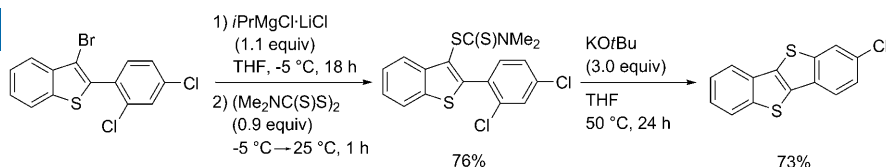
A. V. Cherepanov, C. Glaubitz,
H. Schwalbe* — 4747–4750

High-Resolution Studies of Uniformly
 ^{13}C , ^{15}N -Labeled RNA by Solid-State NMR
Spectroscopy



Sulfur Heterocycles

M. Kienle, A. Unsinn,
P. Knochel* 4751–4754



Synthesis of Dibenzothiophenes and Related Classes of Heterocycles by Using Functionalized Dithiocarbamates

A round trip: Readily available dithiocarbamates can undergo ring closure to give functionalized sulfur heterocycles (see scheme). These heteroaromatic com-

pounds can be further functionalized by directed almination and subsequently trapped with various electrophiles.

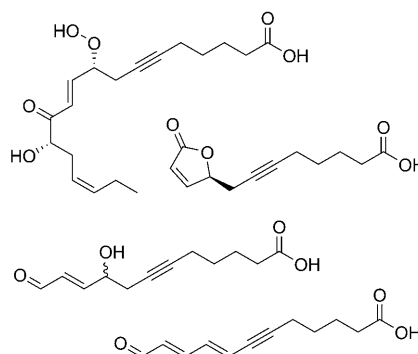
Chemical Defense

M. Rempt, G. Pohnert* 4755–4758



Novel Acetylenic Oxylipins from the Moss *Dicranum scoparium* with Antifeeding Activity against Herbivorous Slugs

A slug stopper: The defensive properties of oxylipins from the moss *Dicranum scoparium* are far more active than required to fend off herbivory by a common slug. The precursor-guided structure elucidation of seven novel and several known unusual oxylipins was supported by chemometric data mining.

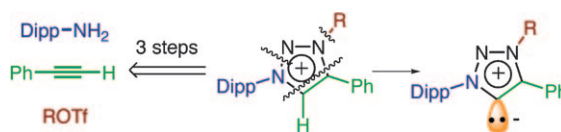


Stable Carbenes

G. Guisado-Barrios, J. Bouffard,
B. Donnadieu, G. Bertrand* 4759–4762



Crystalline 1*H*-1,2,3-Triazol-5-ylidenes: New Stable Mesoionic Carbenes (MICs)



Click makes MICs: A short modular synthesis allows the preparation of novel stable heterocycles that feature a lone pair of electrons on a carbon center. The donor properties of these mesoionic com-

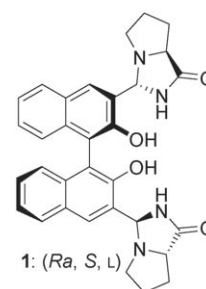
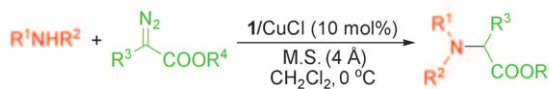
pounds are greater than those of classical N-heterocyclic carbenes; they are accessible by deprotonation of the corresponding conjugate acids using comparatively mild bases.

Asymmetric Catalysis

Z. R. Hou, J. Wang, P. He, J. Wang,
B. Qin, X. H. Liu, L. L. Lin,
X. M. Feng* 4763–4766



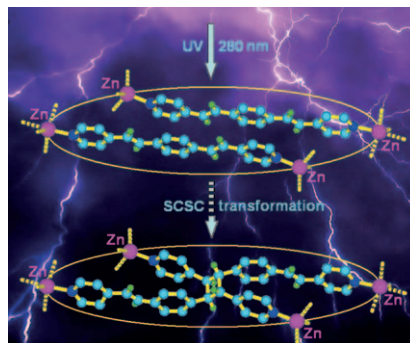
Highly Enantioselective Insertion of Carbenoids into N–H Bonds Catalyzed by Copper(I) Complexes of Binol Derivatives



Secondary amines do it too! Catalytic asymmetric insertion of α -diazoesters in the N–H bond of differently substituted amines has been successfully achieved (see scheme; M.S. = molecular sieves).

For a wide substrate scope, excellent enantioselectivities (up to 98% ee) and high yields (up to 99%) were obtained under mild reaction conditions.

The crystal method: Single-crystal-to-single-crystal (SCSC) transformations of two 3D coordination polymers, $\{[\text{Zn}_4(\mu_3\text{-OH})_2(5\text{-sipa})_2(1,4\text{-bpeb})_2]\cdot 4\text{H}_2\text{O}\}_n$ (see picture; C pale blue, N dark blue, H green) and an analogous cadmium species, gave rise to corresponding linked 3D coordination polymers through photochemical $[2+2]$ cycloaddition reactions.



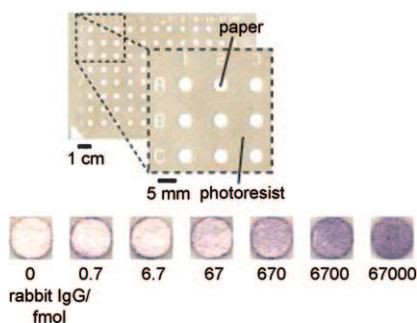
Structural Transformations

D. Liu, Z. G. Ren, H. X. Li, J. P. Lang,*
N. Y. Li, B. F. Abrahams — 4767–4770

Single-Crystal-to-Single-Crystal Transformations of Two Three-Dimensional Coordination Polymers through Regioselective $[2+2]$ Photodimerization Reactions



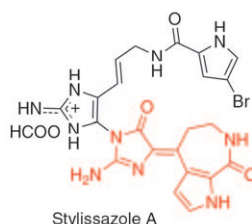
Paper works: Paper-based indirect ELISA (see picture) has been demonstrated through the detection of rabbit IgG and the HIV-1 envelope antigen gp41. This technique combines the sensitivity and specificity of ELISA with the low cost and ease-of-use of paper-based platforms.



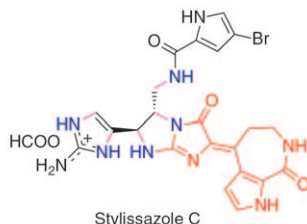
Clinical Analytics

C.-M. Cheng, A. W. Martinez,
J. Gong, C. R. Mace, S. T. Phillips,
E. Carrilho, K. A. Mirica,
G. M. Whitesides* — 4771–4774

Paper-Based ELISA



Stylissazole A



Stylissazole C

No cramping this “styl”: The three title compounds, dimeric pyrrole-2-aminoimidazole alkaloids, were isolated from the marine sponge *Stylissa carteri* collected in the Solomon Islands. The isolated

compounds are exclusively N–C-bonded “dimers”, which indicates a different mode of dimerization and adds another dimension to the molecular diversity of pyrrole-2-aminoimidazole alkaloids.

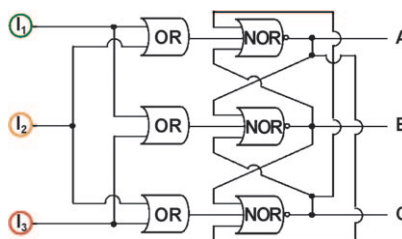
Structure Elucidation

K. Patel, R. Laville, M.-T. Martin, S. Tilvi,
C. Moriou, J.-F. Gallard, L. Ermolenko,
C. Debitus, A. Al-Mourabit* — 4775–4779

Unprecedented Stylissazoles A–C from *Stylissa carteri*: Another Dimension for Marine Pyrrole-2-aminoimidazole Metabolite Diversity



Flip-flopping away: Multivalue random access memory can be achieved using electrically addressable Os^{2+} -based multilayers. The controllable optical properties of the multilayers allow the construction of memory devices that are able to store up to five different states that depend on the given electrical inputs (see picture). The functions of the devices can be represented by sequential logic circuits that are equivalent to flip-flop and flip-flap-flop devices.



Molecular Logic

G. de Ruiter, L. Motiei,
J. Choudhury, N. Oded,
M. E. van der Boom* — 4780–4783

Electrically Addressable Multistate Volatile Memory with Flip-Flop and Flip-Flap-Flop Logic Circuits on a Solid Support

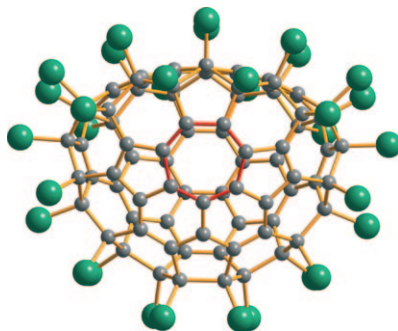


Chlorinated Fullerenes

I. N. Ioffe, C. Chen, S. Yang, L. N. Sidorov,
E. Kemnitz, S. I. Troyanov* – 4784–4787



Chlorination of C_{86} to $C_{84}Cl_{32}$ with
Nonclassical Heptagon-Containing
Fullerene Cage Formed by Cage Shrinkage



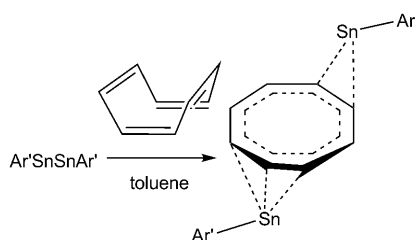
Shrunk fullerene: An unexpected heptagon-containing C_{84} fullerene cage was found in $C_{84}Cl_{32}$, which was formed, in addition to $C_{86}(16)Cl_{28}$, by chlorination of $C_{86}(16)$ with VCl_4 . Comparison of the structures of $C_{84}Cl_{32}$ (see picture; C gray, Cl green; red bonds highlight the heptagon) and $C_{86}(16)Cl_{28}$ and theoretical calculations suggest that cage shrinkage occurs by removal of a C_2 unit from the corannulene-like fragment of the $C_{86}(16)$ cage.

E–E Triple Bonds

O. T. Summerscales, X. Wang,
P. P. Power* – 4788–4790



Cleavage of the Sn–Sn Multiple Bond in a
Distannyne by Cyclooctatetraene:
Formation of the π -Bound
Inverse Sandwich Complex
[$(Ar'Sn)_2(\mu_2-\eta^2:\eta^3-cot)$]



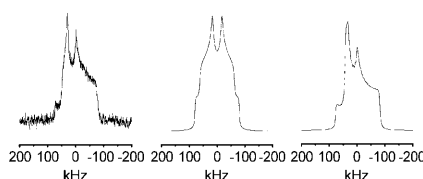
The adventures of tin-tin: The activation of cyclooctatetraene by a distannyne results in complete $Sn=Sn$ bond cleavage and formation of a π -bound planar aromatic C_8H_8 ring in an inverse sandwich complex (see scheme; $Ar' = C_6H_3-2,6-(C_6H_3-2,6-iPr_2)_2$)

Metal–Organic Frameworks

D. I. Kolokolov, H. Jobic,* A. G. Stepanov,
V. Guillermin, T. Devic, C. Serre,
G. Férey – 4791–4794



Dynamics of Benzene Rings in MIL-53(Cr)
and MIL-47(V) Frameworks Studied by
 2H NMR Spectroscopy



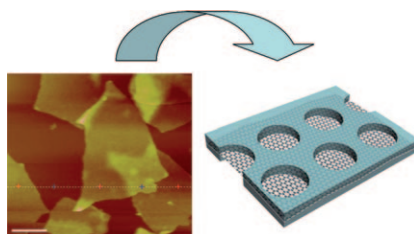
Rotational dynamics of benzene rings in the flexible MIL-53 and rigid MIL-47 frameworks was investigated by 2H NMR spectroscopy. In both cases, 180° flips are observed, and the flipping rate is higher in MIL-53. To simulate experimental spectra (left), consideration of the quadrupolar interaction alone is not sufficient (middle); the paramagnetic effect must also be taken into account (right).

Graphene-Based Nanosheets

S. Yang, X. Feng,* L. Wang, K. Tang,
J. Maier, K. Müllen* – 4795–4799

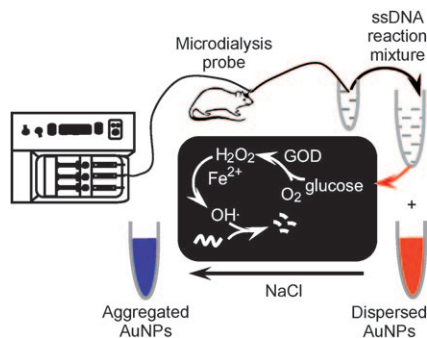


Graphene-Based Nanosheets with a
Sandwich Structure



A bottom-up approach was employed for the large-scale production of 2D graphene-based nanosheets which have a sandwich structure and consist of silica, carbon, and metal or metal oxide (see picture). These nanosheets exhibit many unique features such as a large aspect ratio, high surface area, and high monodispersibility, which render them suitable for broad application in catalysis, sensors, and batteries.

A gold-based assay: By taking advantage of the unique optical properties of gold nanoparticles (AuNPs) and the cascade reactions of glucose, a simple but effective method has been successfully developed for the direct colorimetric visualization of glucose in the rat brain. GOD = glucose oxidase.



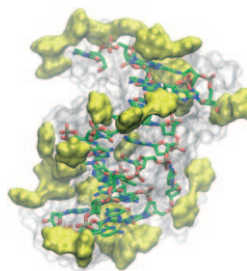
Cerebral Glucose Detection

Y. Jiang, H. Zhao, Y. Lin, N. Zhu, Y. Ma, L. Mao* — 4800–4804

Colorimetric Detection of Glucose in Rat Brain Using Gold Nanoparticles



An unfolding story: Simulations exceeding the microsecond timescale and the introduction of a co-solvent were used to characterize the pathways of the unfolding of a short DNA duplex. Two main pathways are detected involving different substrates. Once unfolding is reached the DNA adopts compact structures different from a random-coil distribution (see picture).



DNA Unfolding

A. Perez, M. Orozco* — 4805–4808

Real-Time Atomistic Description of DNA Unfolding

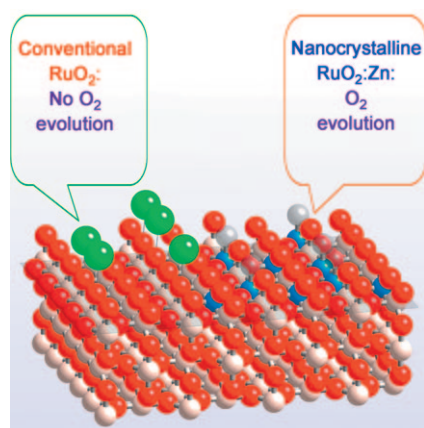


Bound to be active: The solution structure of tubulin-bound tubulysin A is determined from transferred NOE data (see picture; blue N, red O, yellow S, green C), and this bioactive conformation is compared to the unbound conformation. The binding site on tubulin is examined on the basis of the interligand NOEs observed between epothilone A and tubulysin A in the presence of tubulin.

Conformation Analysis

K. Kubicek, S. K. Grimm, J. Orts, F. Sasse, T. Carlomagno* — 4809–4812

The Tubulin-Bound Structure of the Antimitotic Drug Tubulysin



Controlling gas emissions: Versatile control of the selectivity of an oxide electrocatalyst in the oxygen- and chlorine-evolution reactions was demonstrated by Zn substitution in RuO_2 (see picture: O red, Cl green, Zn blue, Ru white). The incorporation of Zn into the rutile structure alters the cation sequence along the [001] direction and modifies the structure of the active sites for both gas-evolution processes.

Electrocatalysis

V. Petrykin, K. Macounova, O. A. Shlyakhtin, P. Krtil* — 4813–4815

Tailoring the Selectivity for Electrocatalytic Oxygen Evolution on Ruthenium Oxides by Zinc Substitution

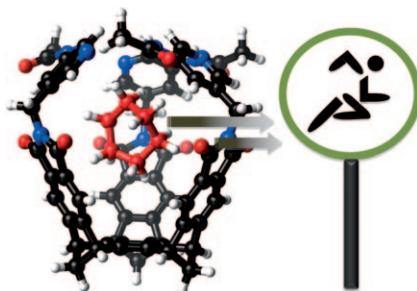


Encapsulation and Reactivity

X. Bao, S. Rieth, S. Stojanović,
C. M. Hadad, J. D. Badjić* — 4816–4819



Molecular Recognition of a Transition State



An inside job: The conformational inter-conversion of cyclohexane occurs at a higher rate in the interior of gated molecular baskets (see picture) than in bulk free solvent or a vacuum. The acceleration results from more favorable noncovalent bonding, and hence stabilization of the transition state, of the encapsulated compound.

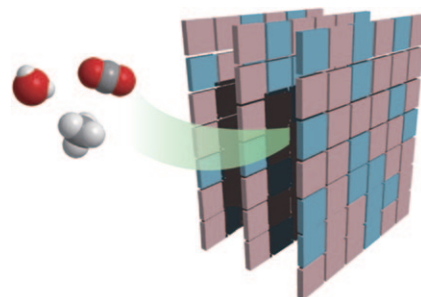
Coordination Polymers

T. Fukushima, S. Horike,* Y. Inubushi,
K. Nakagawa, Y. Kubota, M. Takata,
S. Kitagawa* — 4820–4824



Solid Solutions of Soft Porous Coordination Polymers: Fine-Tuning of Gas Adsorption Properties

My flexible friend: Separation of a CO₂/CH₄ mixture was optimized by varying the composition of solid solutions of interdigitated 2D frameworks comprising two different isophthalate ligands (see picture). The characteristics of the solid solutions were dependent on the ligand ratio, which influenced the inherent flexibility and therefore the adsorption properties of the frameworks.



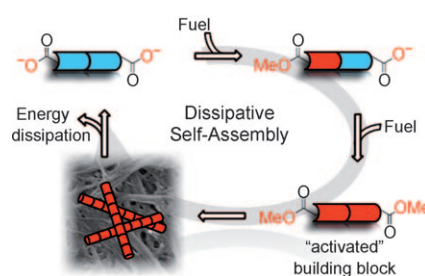
Self-Organization

J. Boekhoven, A. M. Brizard,
K. N. K. Kowlgi, G. J. M. Koper,
R. Eelkema, J. H. van Esch* — 4825–4828



Dissipative Self-Assembly of a Molecular Gelator by Using a Chemical Fuel

Fueling the future: A fibrillar network (red fibers, see figure) is formed from an activated building block (red), which is obtained from a synthetic gelator (blue) in a dissipative self-assembly process that is fueled by an alkylating agent. When the available energy is depleted, the system reverts to its thermodynamic equilibrium, that is, an isotropic solution.



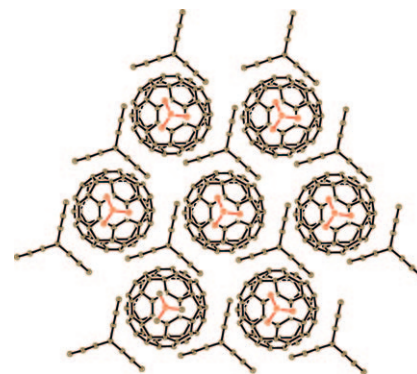
Organic Metals

D. V. Konarev,* S. S. Khasanov, A. Otsuka,
M. Maesato, G. Saito,*
R. N. Lyubovskaya — 4829–4832



A Two-Dimensional Organic Metal Based on Fullerene

The first fullerene organic metal: (MDABCO⁺)₂TPC·(C₆₀^{•-}), which has two-dimensional layers with a honeycomb arrangement of C₆₀^{•-} (see picture), is a fascinating example of a material composed of only light elements (C, H, N); it adopts a metallic state down to 1.9 K.



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).

WILEY InterScience®
DISCOVER SOMETHING GREAT

"Hot Papers" are chosen by the Editors for their importance in a rapidly evolving field of high current interest. A preview with the graphical abstracts of these articles can be found on the *Angewandte Chemie* homepage in Wiley InterScience at www.angewandte.org.

All articles in *Angewandte Chemie* are published online several weeks ahead of print. They are found under the "EarlyView" link on the journal's homepage in Wiley InterScience.

Service

Spotlight on Angewandte's Sister Journals _____ 4700–4702

Keywords _____ 4834

Authors _____ 4835

Preview _____ 4837

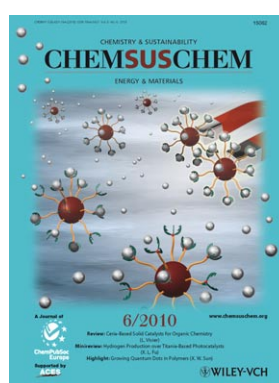
Check out these journals:



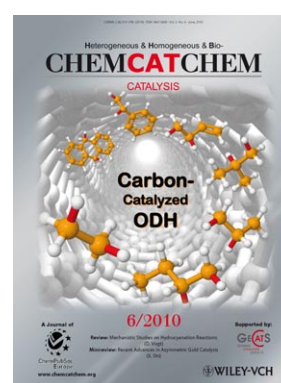
www.chemasianj.org



www.chemmedchem.org



www.chemsuschem.org



www.chemcatchchem.org