

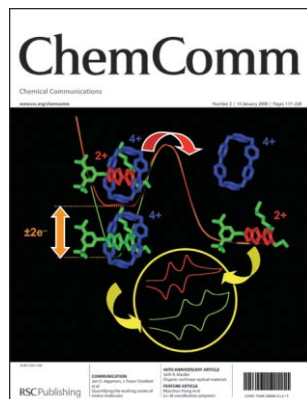
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Cover

See Jan O. Jeppesen, J. Fraser Stoddart *et al.*, page 144.

Charged with the energy of electrostatic repulsion, a mechanically-interlocked [2]rotaxane can overcome its barrier to freedom within two minutes.

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CHEMICAL TECHNOLOGY

T1

Chemical Technology highlights the latest applications and technological aspects of research across the chemical sciences.

Chemical Technology

January 2006/Volume 3/Issue 1

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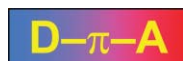
40TH ANNIVERSARY ARTICLE

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Organic nonlinear optical materials: where we have been and where we are going

Seth R. Marder

Organic nonlinear optical materials for electro-optical and multiphoton absorption applications have improved significantly in recent years based upon the development of structure-property relationships on the molecular level.



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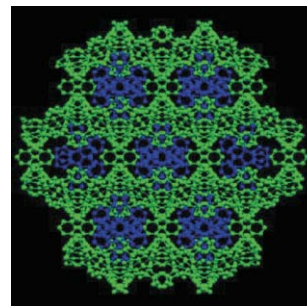
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Lanthanide–transition metal coordination polymers based on multiple *N*- and *O*-donor ligands

Youfu Zhou, Maochun Hong* and Xintao Wu

A series of lanthanide–transition metal (Ln–M) coordination polymers were synthesized with various structure motifs (such as multi-encapsulated cations within a charged cavity and high-nuclear heterometallic clusters) and rich magnetic properties.



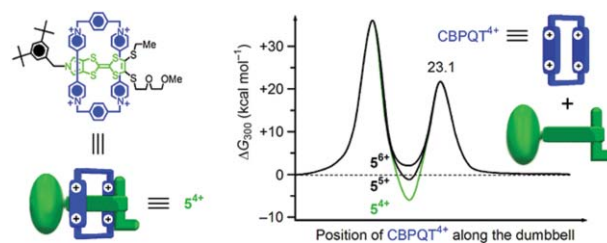
COMMUNICATIONS

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Quantifying the working stroke of tetrathiafulvalene-based electrochemically-driven linear motor-molecules

Sune Nygaard, Bo W. Laursen, Amar H. Flood, Camilla N. Hansen, Jan O. Jeppesen* and J. Fraser Stoddart*

A highly constrained [2]rotaxane, constructed in such a way that the tetracationic cyclobis(paraquat-*p*-phenylene) ring is restricted to reside on a monopyrrolotetrathiafulvalene unit, has been synthesized and characterized. This design allows the deslipping free energy barrier for the tetracationic ring in all three redox states of the rotaxane to be determined.

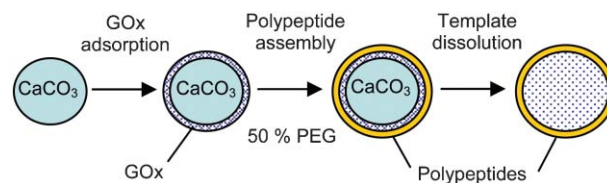


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High-capacity functional protein encapsulation in nanoengineered polypeptide microcapsules

Zheng-liang Zhi and Donald T. Haynie*

Addition of polyethylene glycol to aqueous assembly solutions of oppositely charged polypeptides enables high-capacity “loading” of functional glucose oxidase (GOx) in biocompatible microcapsules by template-supported layer-by-layer nanoassembly.

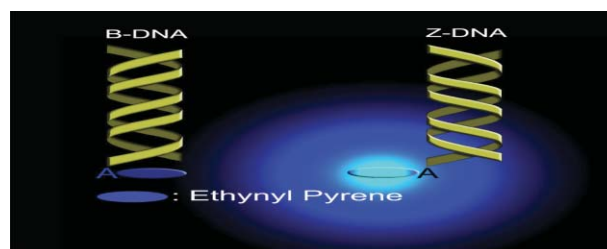


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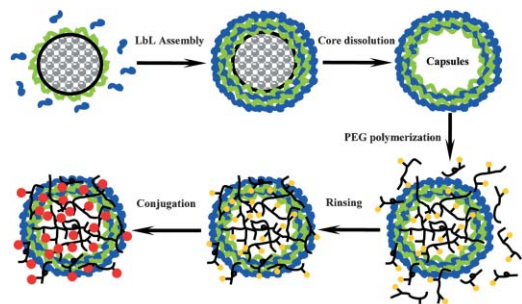
Probing the B-to-Z-DNA duplex transition using terminally stacking ethynyl pyrene-modified adenosine and uridine bases

Young Jun Seo and Byeang Hyeon Kim*

Pyrene-modified adenosine and uridine bases located in the dangling positions of G,C-alternating oligodeoxynucleotides allow us to monitor the B-to-Z-DNA transition visually.



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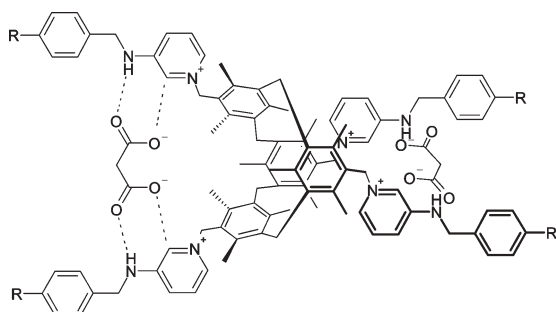


Synthesis and functionalization of monodisperse poly(ethylene glycol) hydrogel microspheres within polyelectrolyte multilayer microcapsules

Huiguang Zhu* and Michael J. McShane

Polyelectrolyte multilayer microcapsules were used as templates to prepare monodisperse poly(ethylene glycol) (PEG) hydrogel microspheres, which can react with amine-bearing molecules.

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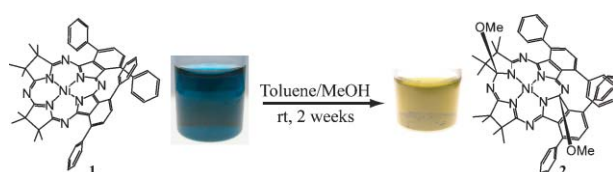


Modular assembly of a preorganised, ditopic receptor for dicarboxylates

Maria H. Filby, Terry D. Humphries, David R. Turner, Ritu Katak, Jaanus Kruusma and Jonathan W. Steed*

Two types of calix[4]arene derived hosts for anions with, respectively, 1,3-alternate and cone conformations have been prepared. The 1,3-alternate system binds dicarboxylate anions in a ditopic manner while the cone compounds are deprotonated by carboxylates.

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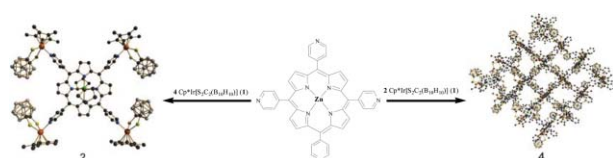


Skeletal modification of a non-planar phthalocyanine analogue under very mild conditions

Takamitsu Fukuda, Yusuke Ogi and Nagao Kobayashi*

A sterically congested tetraphenyl-substituted dibenzo-tetraazaisobacteriochlorinato nickel derivative (**1**) reacts with methanol under very mild conditions, leading to the formation of a bis-methoxy-substituted derivative (**2**).

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Porphyrin-carborane organometallic assemblies based on 1, 2-dicarba-closo-dodecaborane (**12**) ligands

Jian-Qiang Wang, Chun-Xia Ren, Lin-Hong Weng and Guo-Xin Jin*

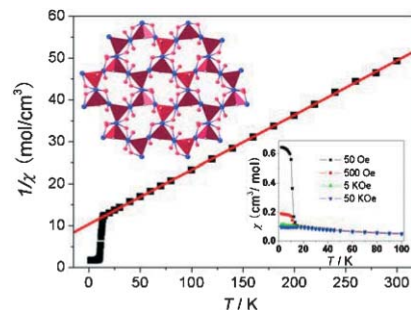
The supramolecular complexes $\{(Zn-TPyP)[Cp^*Ir\{S_2C_2(B_{10}H_{10})\}]_4(THF)_2\}$ (**2**), $\{(Cu-TPyP)[Cp^*Ir\{S_2C_2(B_{10}H_{10})\}]_4(THF)_2\}$ (**3**) and $\{(Zn-TPyP)[Cp^*Ir\{S_2C_2(B_{10}H_{10})\}]_2 \cdot 6(CHCl_3)\}_n$ (**4**) were synthesized and characterized by X-ray crystallography.

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Coexistence of spin frustration and long-range magnetic ordering in a triangular $\text{Co}^{\text{II}}(\mu_3\text{-OH})$ -based two-dimensional compound

Yan-Zhen Zheng, Ming-Liang Tong, Wei-Xiong Zhang and Xiao-Ming Chen*

A novel two-dimensional compound $[\text{Co}_3(\mu_3\text{-OH})_2(1,2\text{-chdc})_2]_\infty$ (1,2-chdc = *trans*-1,2-cyclohexane-dicarboxylate) comprising triangular arrays of $\text{Co}^{\text{II}}(\mu_3\text{-OH})$ affording a Kagomé-like lattice exhibits the coexistence of spin frustration and long-range magnetic ordering.

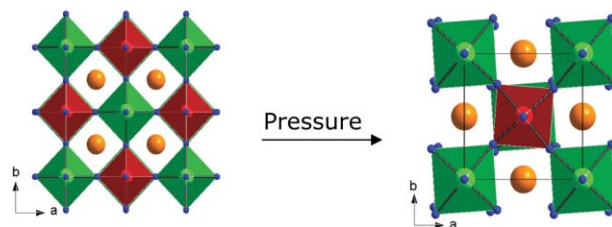


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Pressure induced octahedral tilting distortion in Ba_2YTaO_6

Michael W. Lufaso, René B. Macquart, Yongjae Lee, Thomas Vogt and Hans-Conrad zur Loye*

The first example of a pressure induced octahedral tilting distortion in a double perovskite phase was observed during structural characterization of Ba_2YTaO_6 using high-pressure synchrotron X-ray powder diffraction.

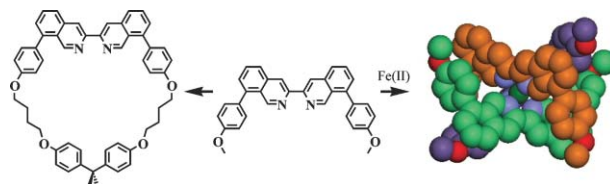


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Sterically non-hindering endocyclic ligands of the bi-isoquinoline family

Fabien Durola, Jean-Pierre Sauvage* and Oliver S. Wenger

8,8'-Disubstituted 3,3'-bi-isoquinoline is an endocyclic but non-sterically hindering ligand.

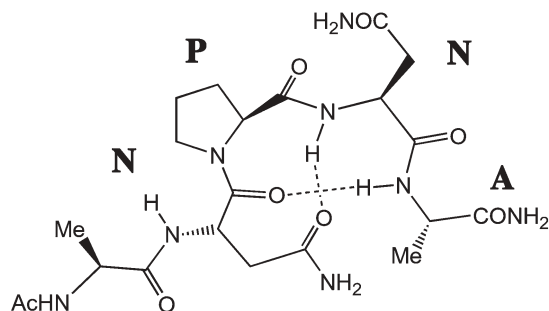


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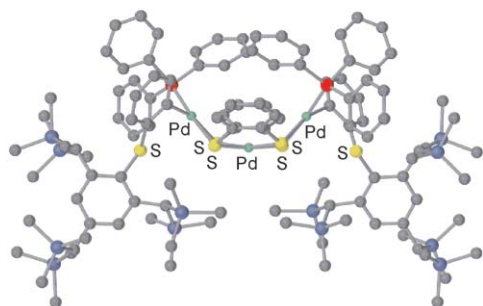
Crystal structure of an NPNA-repeat motif from the circumsporozoite protein of the malaria parasite *Plasmodium falciparum*

Arin Ghasparian, Kerstin Moehle, Anthony Linden and John A. Robinson*

The NPNA repeat motif adopts a type-I β -turn stabilized by two hydrogen bonds, as seen in the crystalline state in the synthetic peptide Ac-Ala-Asn-Pro-Asn-Ala-NH₂.



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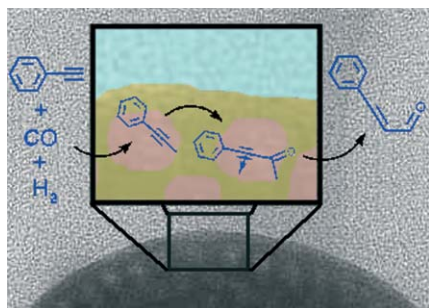


Unusual carbon–sulfur bond cleavage in the reaction of a new type of bulky hexathioether with a zerovalent palladium complex

Daisuke Shimizu, Nobuhiro Takeda and Norihiro Tokitoh*

Unusual C(aryl)–S bond cleavage was observed in the reaction of a novel, bulky hexathioether with Pd(PPh₃)₄ to afford a unique tripalladium complex.

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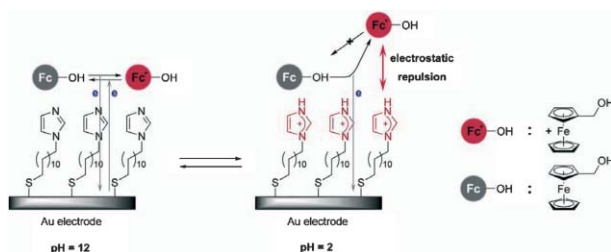


Highly regioselective terminal alkynes hydroformylation and Pauson–Khand reaction catalysed by mesoporous organised zirconium oxide based powders

Frédéric Goettmann, Pascal Le Floch* and Clément Sanchez*

Zirconia–silica mesoporous powders act as heterogeneous catalysts for both alkyne hydroformylation and Pauson–Khand reaction and yield regioselectivities opposite to those usually observed.

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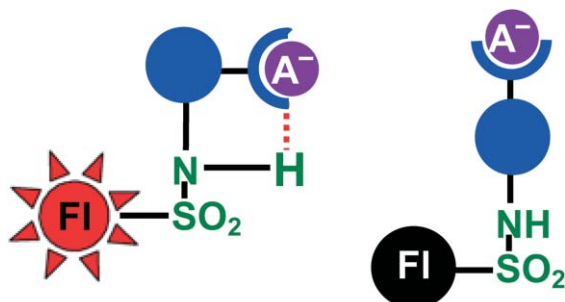


pH-Dependent rectification in self-assembled monolayers based on electrostatic interactions

Seongpil Hwang, Young Shik Chi, Bang Sook Lee, Sang-gi Lee,* Insung S. Choi* and Juhyoun Kwak*

Asymmetric electrostatic interactions dependent on pH between the redox molecules and the terminal group on the top of the self-assembled monolayer (SAM) afford control of the electron transfer property of the SAM having the imidazole terminal group.

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Fluorescence modulation in anion sensing by introducing intramolecular H-bonding interactions in host–guest adducts

Yun Mi Chung, Balamurali Raman, Dae-Sik Kim and Kyo Han Ahn*

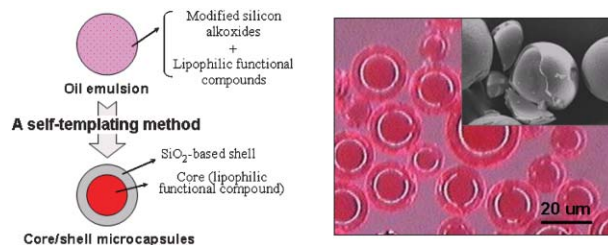
Intramolecular H-bonding stabilization of anion–ionophore adducts leads to a dramatic modulation of fluorescence, from quenching to enhancement.

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Core/shell silica-based *in-situ* microencapsulation: A self-templating method

Bok Yeop Ahn, Sang Il Seok,* In Chan Baek and Suk-In Hong

Core/shell silica-based microcapsules were synthesized by a self-templating method in an O/W emulsion system from modified silicon alkoxides. The *in-situ* process provides a versatile and effective route for encapsulating lipophilic functional compounds with high purity.

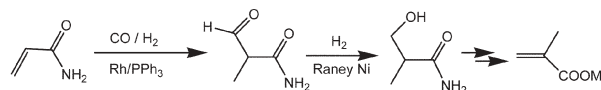


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A highly selective synthesis of 3-hydroxy-2-methylpropionamide involving a one-pot tandem hydroformylation–hydrogenation sequence

Luis García, Carmen Claver, Montserrat Diéguez* and Anna M. Masdeu-Bultó*

3-Hydroxy-2-methylpropionamide, an important intermediate in the synthesis of methyl methacrylate, has been obtained with excellent conversion from acrylamide by a tandem hydroformylation–hydrogenation sequence.

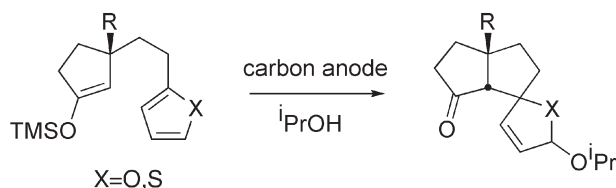


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Electrochemical annulation of five-membered rings through dearomatization of furans and thiophenes

Jeffrey B. Sperry, Ion Ghiviriga and Dennis L. Wright*

A new methodology for the annulation of five-membered carbocyclic rings onto enones through the dearomatizing electrochemical cyclization of furans and thiophenes has been developed.

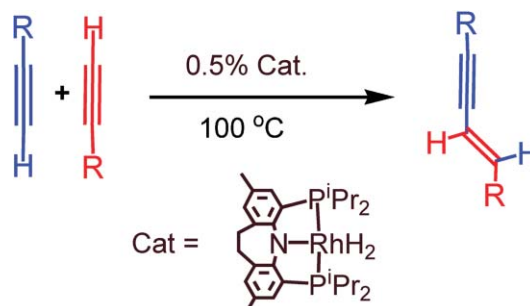


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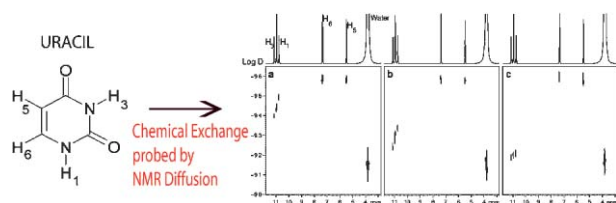
Skeletal change in the PNP pincer ligand leads to a highly regioselective alkyne dimerization catalyst

Wei Weng, Chengyun Guo, Remle Çelenligil-Çetin, Bruce M. Foxman and Oleg V. Ozerov*

A Rh complex of a bulky PNP pincer ligand is a robust catalyst for the dimerization of terminal alkynes and highly selective of the *trans*-enyne product.



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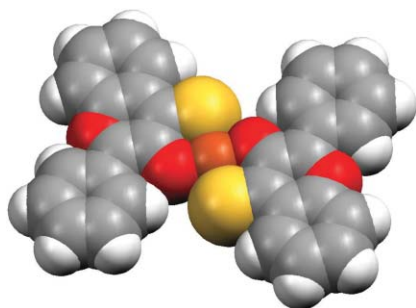


Determining chemical exchange rates of the uracil labile protons by NMR diffusion experiments

Pierre Thureau, Bernard Ancian,* Stéphane Viel and André Thévand

Interesting properties of the labile protons of uracil are highlighted by diffusion NMR experiments, which provide a rapid and precise method for studying chemical exchange.

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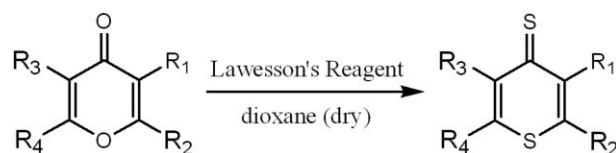


Flavothionato metal complexes: implications for the use of hydroxyflavothiones as green pesticides

Ba L. Tran and Seth M. Cohen*

Metal ions are found to stabilize the photodegradation of 3-hydroxyflavothione, a possible candidate as an environmentally benign pesticide.

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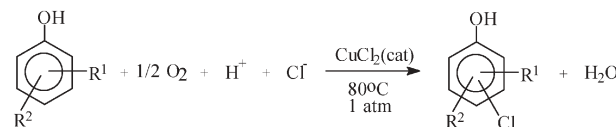


A novel heterocyclic atom exchange reaction with Lawesson's reagent: a one-pot synthesis of dithiomaltol

Daniel Brayton, Faith E. Jacobsen, Seth M. Cohen and Patrick J. Farmer*

A one-pot reaction of maltol with Lawesson's reagent generates dithiomaltol, a thiopyran-4-thione, *via* an unusual heterocyclic atom exchange (HCAE) reaction; only pyrones with proton or aliphatic substituents undergo the HCAE substitution.

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Novel highly selective catalytic oxychlorination of phenols

Luciano Menini and Elena V. Gusevskaya*

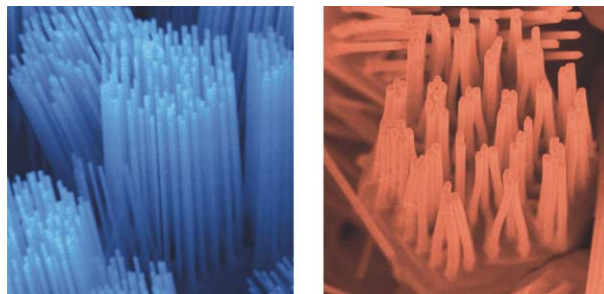
The highly selective oxychlorination of various phenols catalyzed by CuCl_2 under mild conditions, in which chloride ions are used as chlorinating agents and dioxygen as a final oxidant, has been developed.

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Crystal orientation-ordered ZnO nanorod bundles on hexagonal heads of ZnO microcones: epitaxial growth and self-attraction

Xinhai Han, Guanzhong Wang,* Lei Zhou and J. G. Hou

We demonstrate a preferential nucleation, epitaxial growth, and self-attraction of crystal orientation-ordered ZnO nanorod bundles on (0001) plane of single-crystal ZnO microcones.

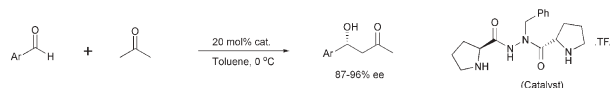


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Protonated *N'*-benzyl-*N'*-prolyl proline hydrazide as highly enantioselective catalyst for direct asymmetric aldol reaction

Chuanling Cheng, Jian Sun,* Chao Wang, Yu Zhang, Siyu Wei, Fan Jiang and Yundong Wu*

A proline hydrazide derivative has been developed for the first time as a highly enantioselective organocatalyst. Protonated *N'*-benzyl-*N'*-prolyl proline hydrazide catalyzes the asymmetric direct aldol reaction of aromatic aldehydes and ketones with up to 96% ee.

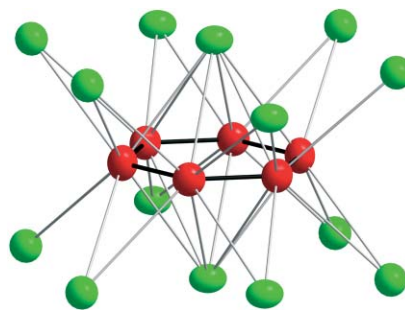


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No aromaticity of P_6^{4-} observed *via* solid state ^{31}P -NMR spectroscopy

Florian Kraus, Jörn Schmedt auf der Günne, Brian F. DiSalle and Nikolaus Korber*

The solid state NMR spectra of the binary alkali hexaphosphides Rb_4P_6 and Cs_4P_6 unambiguously show the P_6^{4-} anion not to be aromatic.

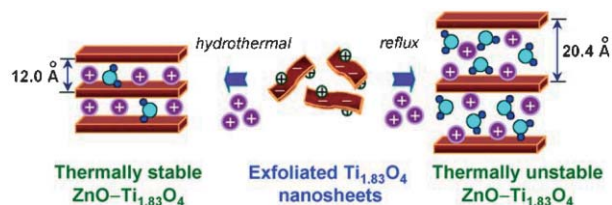


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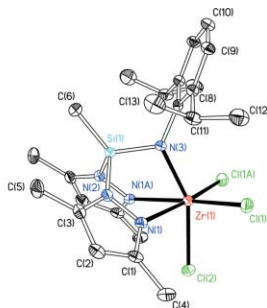
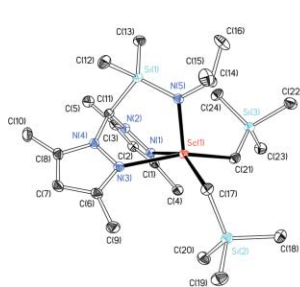
Layered titanate–zinc oxide nano hybrids with mesoporosity

Tae Woo Kim, Su Gil Hur, Seong-Ju Hwang* and Jin-Ho Choy*

Zinc oxide-layered titanate nano hybrids with a 1 : 1 ordered heterostructure have been synthesized for the first time by reassembling exfoliated titanate nanosheets in the sol solution of zinc acetate under hydrothermal or reflux conditions.



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A novel transformation of a zirconium imido compound and the development of a new class of N₃ donor heteroscorpionate ligand

Robert G. Howe, Cara S. Tredget, Sally C. Lawrence, Suparabhorn Subongkoj, Andrew R. Cowley and Philip Mountford*

Reaction of $[\text{Zr}_2(\mu\text{-NAr})_2\text{Cl}_4(\text{THF})_4]$ with $\text{MeSi}(\text{Me}_2\text{pz})_3$ gave $[\text{Zr}\{(\text{Me}_2\text{pz})_2\text{Si}(\text{Me})\text{NAr}\}\text{Cl}_3]$, a highly active pre-catalyst for ethylene polymerisation. A general route to N₃ donor heteroscorpionate compounds was achieved *via* $(\text{Me}_2\text{pz})_2\text{CHSi}(\text{Me})_2\text{N}(\text{H})^i\text{Pr}$.

ADDITIONS AND CORRECTIONS

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Philip A. Gale

Amidopyrroles: from anion receptors to membrane transport agents

Philip A. Gale, Mark E. Light, Beth McNally, Korakot Navakhun, Kate E. Sliwinski and Bradley D. Smith

Co-transport of H⁺/Cl⁻ by a synthetic prodigiosin mimic

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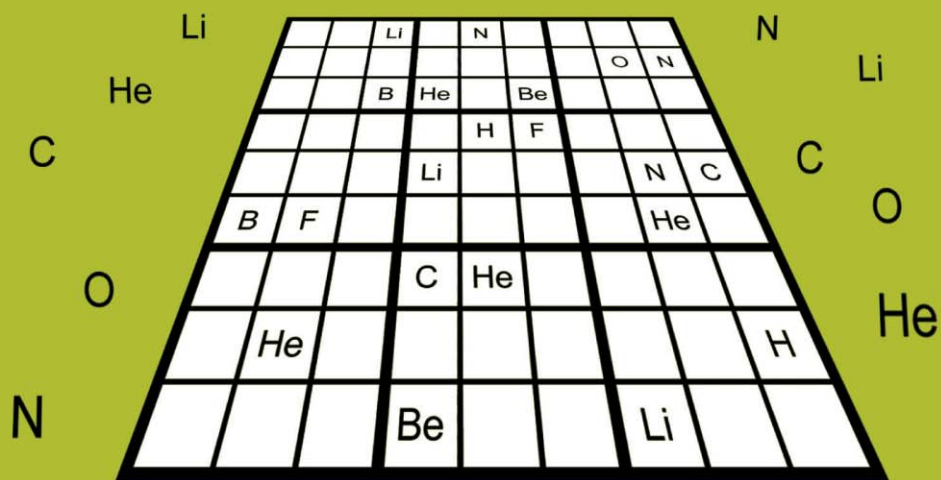
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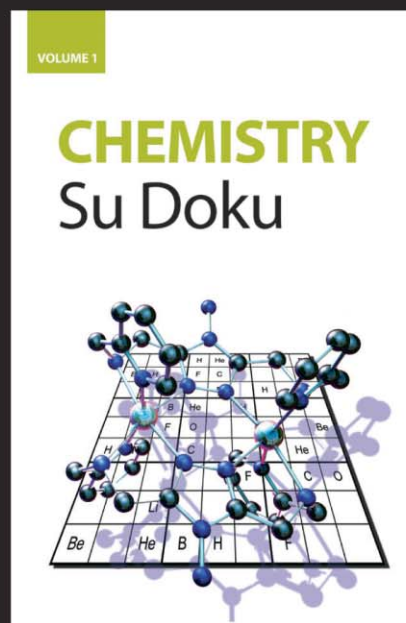


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