**Cover (far left)**

Receptor complexes showing cation-pi interactions. Such interactions may be of significance in biological systems.

Inside cover (left)

A self-assembled metallocupramolecular tetrahedron (edge length approximately 2 nm), binding four $[K(dmf)_3]^+$ -units in its huge internal cavity.

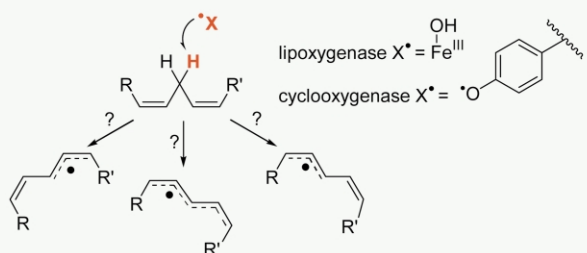
contents

FOCUS ARTICLE

2843

Enzymatic hydrogen atom abstraction from polyunsaturated fatty acids

Chris M. McGinley and Wilfred A. van der Donk*



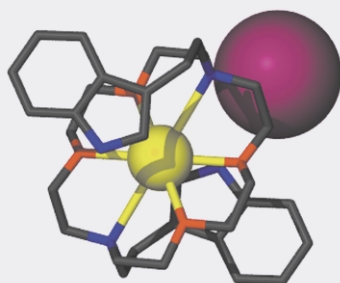
The oxidation of polyunsaturated fatty acids by prostaglandin synthase and the lipoxygenases provides an impressive example of enzymatic control of hydrogen atom abstraction and subsequent oxygenation.

FEATURE ARTICLE

2847

The aromatic sidechains of amino acids as neutral donor groups for alkali metal cations

George W. Gokel*



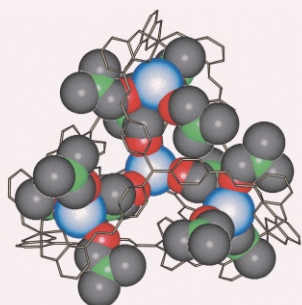
Interactions between neutral pi-donors and sodium or potassium cations, demonstrated here, are potentially important in nature.

COMMUNICATIONS

2854

A metallocupramolecular tetrahedron with a huge internal cavity

Markus Albrecht,* Ingo Janser, Sebastian Meyer, Patrick Weis and Roland Fröhlich



A huge molecular tetrahedral complex forms quantitatively by self-assembly from four ligands $L-H_6$ and four titanium(IV) ions; in the solid state it encapsulates four $\{K(DMF)_3\}^+$ units in its interior.

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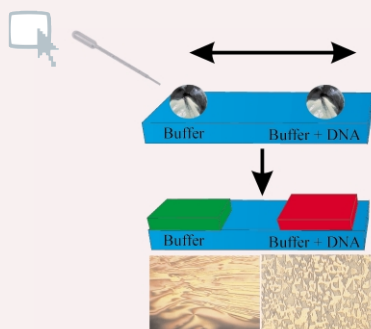
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2856

Novel alignment technique for LCD-biosensors

Johan Hoogboom, Joost Clerx, Matthijs B. J. Otten, Alan E. Rowan,* Theo Rasing* and Roeland J. M. Nolte*

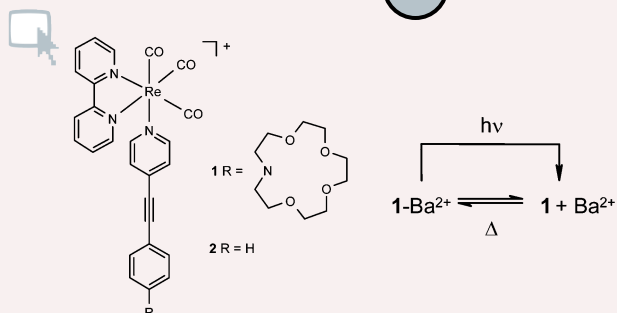


The directional drying of a Tris-EDTA buffer on a PI-ITO surface results in the formation of a well-ordered alignment layer, underpinned by the formation of an extensive hydrogen bond network. The surface ordering is sufficient to give visible alignment of the nematic liquid crystal 5CB. When λ -phage DNA is added to the drying droplet, a cholesteric fan-phase is observed along the path of the drying droplet, making this a simple, yet effective system for the detection of biomolecules.

2858

Photoinduced Ba^{2+} release and thermal rebinding by an azacrown ether linked by an alkynyl pyridine to a (bpy)Re(CO)₃ group

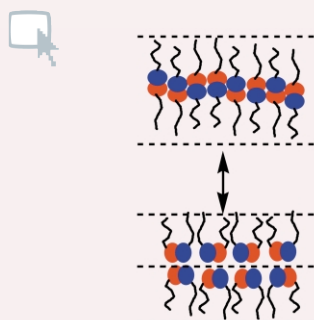
Jared D. Lewis and John N. Moore*



2860

A bilayer to monolayer phase transition in liquid crystal glycolipids

Valérie Molinier, Paul H. J. Kouwer, Yves Queneau,* Juliette Fitremann, Grahame Mackenzie and John W. Goodby*

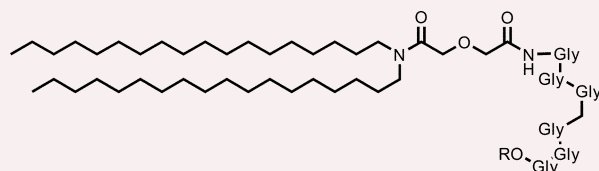


Investigations of the thermotropic liquid-crystalline properties of 6,6'-di-*O*-stearoylsucrose show, for the first time, that glycolipids can exhibit phase transitions within the smectic A phase.

2862

The C-terminal ester of membrane anchored peptide ion channels affects anion transport

Natasha Djedovic, Riccardo Ferdani, Egan Harder, Jolanta Pajewska, Robert Pajewski, Paul H. Schlesinger and George W. Gokel*

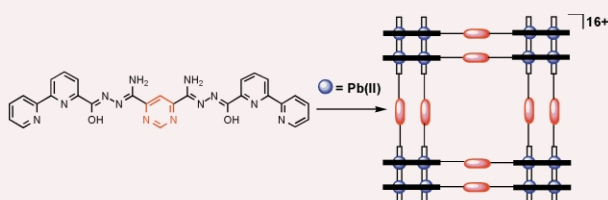


The C-terminal ester residue of heptapeptide anion channels having N-terminal anchor chains affects ion transport and apparently serves as a "secondary" membrane anchor.

2864

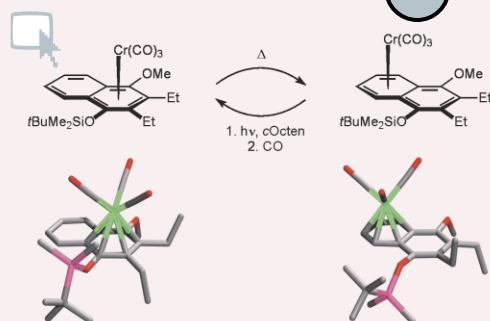
Self-assembly of a unique hexadecanuclear [4 × (2 × 2)]-Pb₁₆ 'grid of grids' type structure

Stuart T. Onions, Anthony M. Frankin, Peter N. Horton, Michael B. Hursthouse and Craig J. Matthews*



The power of ligand and metal ion self-assembly is highlighted by the formation of a unique hexadecanuclear [4 × (2 × 2)] 'grid of grids' type structure with truly nanometric dimensions.

2866

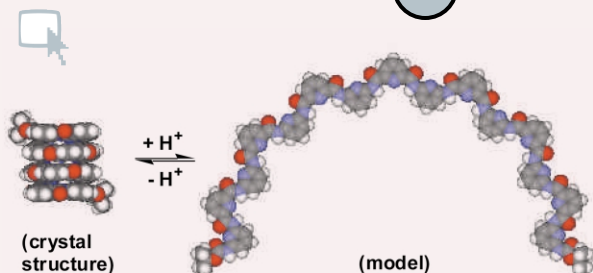


Controlled haptotropic rearrangements – towards a stereospecific molecular switch based on chiral arene chromium complexes

Holger C. Jahr, Martin Nieger and Karl Heinz Dötz*

A stereospecific molecular switch has been designed based on a reversible thermo- or photo-induced haptotropic shift of a $\text{Cr}(\text{CO})_3$ fragment along a naphthoquinone skeleton.

2868

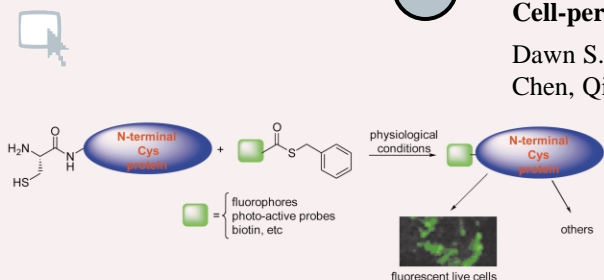


Contraction/extension molecular motion by protonation/deprotonation induced structural switching of pyridine derived oligoamides

Elena Kolomiets, Volker Berl, Ibon Odriozola, Adrian-Mihail Stadler, Nathalie Kyritsakas and Jean-Marie Lehn*

NMR, mass spectrometry and X-ray diffraction studies show reversible structural interconversion between helical and extended forms of pyridine derived oligoamide molecular strands, by simple protonation/deprotonation

2870

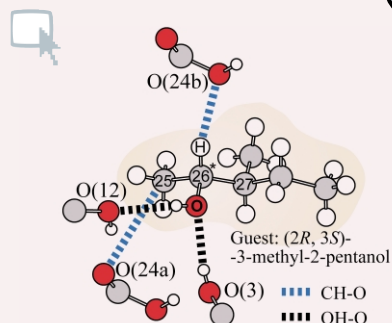


Cell-permeable small molecule probes for site-specific labeling of proteins

Dawn S. Y. Yeo, Rajavel Srinivasan, Mahesh Uttamchandani, Grace Y. J. Chen, Qing Zhu and Shao Q. Yao*

We have successfully synthesized small molecule probes designed for site-specific labeling of N-terminal cysteine-containing proteins expressed in live cells. Their utility for site-specific, covalent modifications of proteins was demonstrated with purified proteins *in vitro*, and with live bacterial cells *in vivo*.

2872

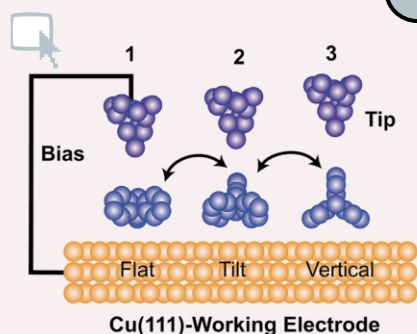


Excellent enantio-selective enclathration of (2R,3S)-3-methyl-2-pentanol in channel-like cavity of 3-epideoxycholeic acid, interpreted by the four-location model for chiral recognition

Kazuaki Kato,* Kazuaki Aburaya, Yasuhito Miyake, Kazuki Sada, Norimitsu Tohnai and Mikiji Miyata*

Pure (2R,3S)-3-methyl-2-pentanol is resolved from the racemates by a steroidal host; an interpretation of the recognition mechanism based on the crystal structure is given.

2874

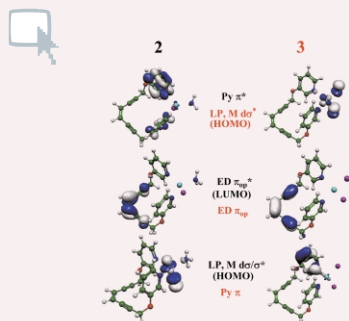


Tuning molecular orientation with STM at the solid/liquid interface

Qing-Min Xu, Mei-Juan Han, Li-Jun Wan,* Chen Wang, Chun-Li Bai,* Bing Dai and Jin-Long Yang

With bias stimulation, the molecules are tuned at different orientations on $\text{Cu}(111)$ surface from flat, to tilt, to vertical. The tuning is completely bias dependent and reversible.

2876

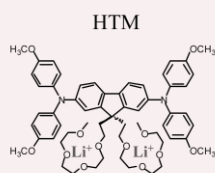


A TDDFT description of the low-energy excited states of copper and zinc metalloenediynes

Aurora E. Clark, Ernest R. Davidson and Jeffrey M. Zaleski*

Time-dependent density functional theory shows that the photoreactivities of copper and zinc metalloenediynes derive from multi-configurational excited states involving the enediyne and pyridine π systems.

2878

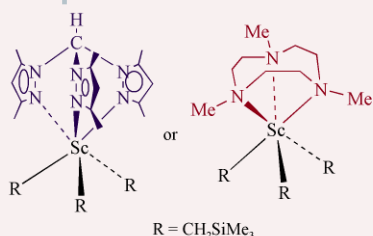


A supramolecular approach to lithium ion solvation at nanostructured dye sensitised inorganic/organic heterojunctions

Taiho Park, Saif A. Haque, Robert J. Potter, Andrew B. Holmes* and James R. Durrant*

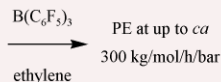
A novel arylamine based hole transporting material (HTM) with tetraethylene glycol (TEG) side groups is reported. Lithium ions solubilised by the TEG groups are employed to modulate interfacial electron transfer reactions at a dye sensitised TiO_2 /HTM interface.

2880



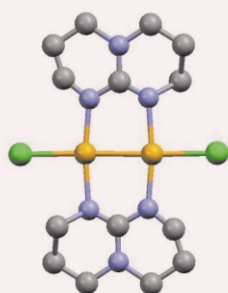
Highly efficient ethylene polymerisation by scandium alkyls supported by neutral *fac*- κ^3 coordinated N_3 donor ligands

Sally C. Lawrence, Benjamin D. Ward, Stuart R. Dubberley, Christopher M. Kozak and Philip Mountford



Reaction of $[\text{M}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ ($\text{M} = \text{Sc}$ or Y) with the neutral *fac*- κ^3 N_3 donor ligands (L) $\text{Me}_3[9]\text{aneN}_3$ or $\text{HC}(\text{Me}_2\text{pz})_3$ gave the corresponding trialkyls $[\text{M}(\text{L})(\text{CH}_2\text{SiMe}_3)_3]$; activation of the scandium congeners with $\text{B}(\text{C}_6\text{F}_5)_3$ in the presence of ethylene afforded highly active polymerisation catalysts.

2882

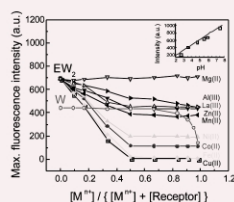
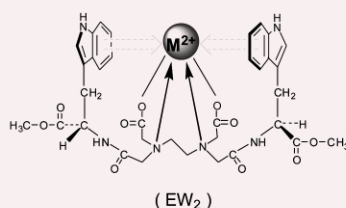


Synthesis and X-ray structures of silver and gold guanidinate-like complexes. A Au(II) complex with a 2.47 Å Au–Au distance

Michael D. Irwin, Hanan E. Abdou, Ahmed A. Mohamed and John P. Fackler, Jr.*

The structure of the first dinuclear Au(II)–N complex, $[\text{Au}(\text{hpp})\text{Cl}]_2$, is described and found to contain the shortest Au–Au bond (2.47 Å) heretofore observed. With Ag(I) a tetranuclear guanidinate-like complex forms.

2884



A rationally designed novel receptor for probing cooperative interaction between metal ions and bivalent tryptophan side chain in solution

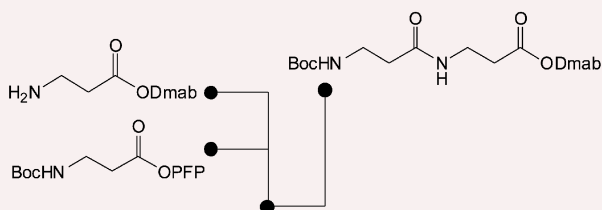
Yitong Li and Chi Ming Yang*

Cooperative interactions between transition metal ions and bivalent tryptophan are identified in water by fluorescence quenching of a novel receptor, EDTA-bis(L-tryptophan methyl ester), which is demonstrated to be highly selective for copper(II) and iron(II).

2886

On-chip separation of peptides prepared within a micro reactor

Vinod George, Paul Watts, Stephen J. Haswell* and Esteban Pombo-Villar

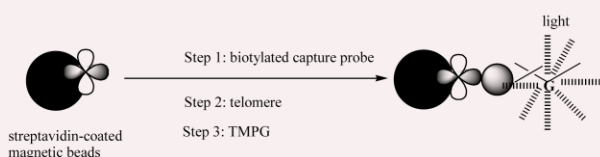


We report that dipeptides may be synthesised and electrophoretically separated from unreacted reagents within an integrated micro reactor.

2888

Magnetic bead-based label-free chemiluminescence detection of telomeres

Jianzhong Lu,* Choiwan Lau and Masaaki Kai*

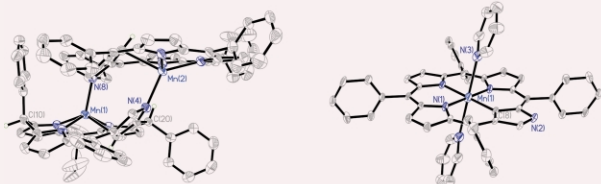


For the first time we report on the detection of telomeres by coupling of the label-free guanine CL detection route with an efficient magnetic isolation of the hybrid.

2890

Manganese N-confused porphyrin reactivity: CH bond activation and meso carbon reduction

John D. Harvey and Christopher J. Ziegler*

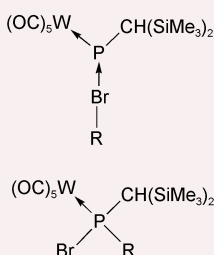


Manganese N-confused porphyrins activate C–C and C–H bonds upon heating or air oxidation; the dimer complex $[\text{Mn}(\text{NCTPP})]_2$ is reduced at two meso positions, and the pyridine coordinated monomer breaks the internal C–H bond upon heating or exposure to oxygen.

2892

Electrophilic terminal phosphinidene complex–Lewis base adducts: Chemistry between carbon–halide bond activation and weak Lewis base adduct formation

Arif Ali Khan, Cathleen Wismach, Peter G. Jones and Rainer Streubel*

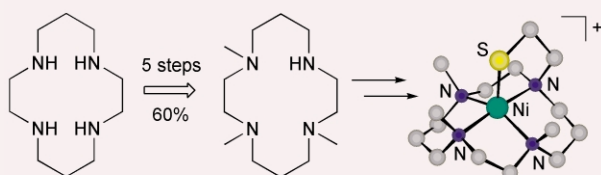


The first comparative study on the reactivity of a transiently formed terminal phosphinidene complex towards various organobromide derivatives is presented and different reaction pathways are highlighted.

2894

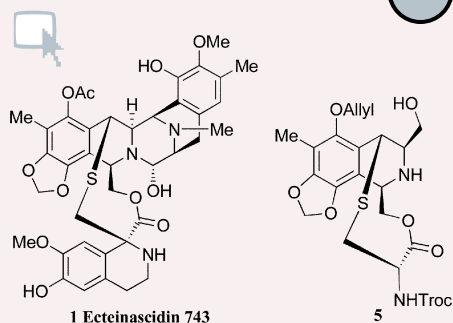
Efficient preparation of 1,4,8-trimethylcyclam and its conversion into a thioalkyl-pendant pentadentate chelate

Jason A. Halfen* and Victor G. Young, Jr.



A facile, high-yield synthesis of 1,4,8-trimethylcyclam is reported. The X-ray crystal structure of a thiolate-pendant derivative illustrates structural perturbations caused by attachment of the sulfur donor to the macrocycle.

2896

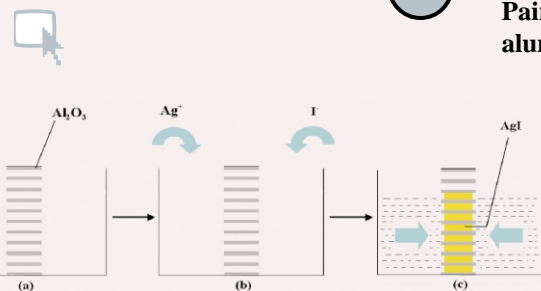


Synthetic studies on ecteinascidin 743: rapid access to the fully functionalized tetrahydroisoquinoline with a bridged 10-membered sulfur containing macrocycle

Michaël De Paolis, Angèle Chiaroni and Jieping Zhu*

Convergent synthesis of tetrahydroisoquinoline **5** featuring key Pictet–Spengler reaction of acid sensitive amino diol and macrocyclization *via* C–S bond formation is described.

2898

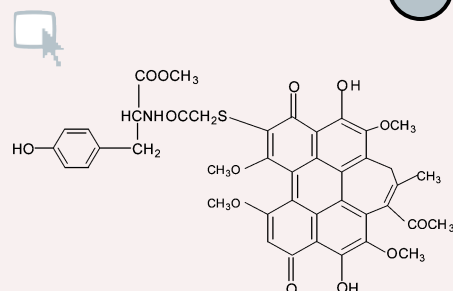


Paired cell for the preparation of AgI nanowires using nanoporous alumina membrane templates

Yuanzhe Piao and Hasuck Kim*

This communication describes a relatively new and simple method for the preparation of AgI nanowires using nanoporous alumina membrane templates which can be easily extended to prepare nanowires of many other inorganic materials.

2900

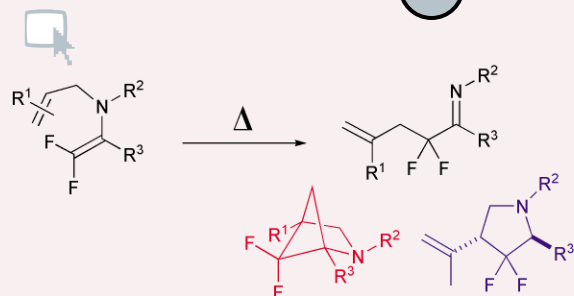


A tyrosine-modified hypocrellin B with affinity for and photodamaging ability towards calf thymus DNA

Sheng Qin Xia, Jia Hong Zhou, Jing Rong Chen, Xue Song Wang* and Bao Wen Zhang*

An enhanced photodamaging ability towards CT-DNA was achieved in a tyrosine-modified hypocrellin B by improving the affinity of the sensitizer to DNA.

2902

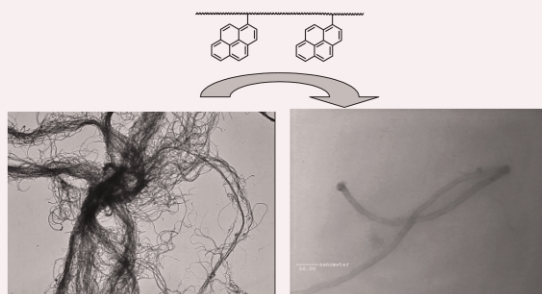


Unusual reactions of *N*-allylic difluoroenamines under thermal conditions

Hideki Amii, Yutaka Ichihara, Takashi Nakagawa, Takeshi Kobayashi and Kenji Uneyama*

N-Allylic difluoroenamines exhibited unusual behaviors under thermal conditions. Heating *N*-allylic difluoroenamines in refluxing xylene afforded not only aza-Claisen rearrangement products, but also 2-azabicyclo[2.1.1]hexanes. In contrast, *N*-prenyl difluoroenamine underwent an ene reaction to give the pyrrolidine as a sole product.

2904

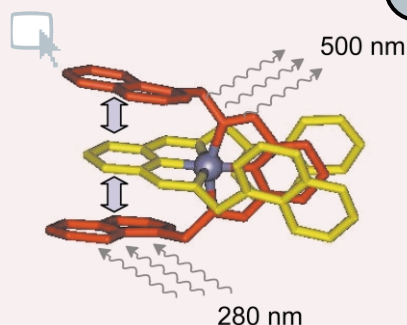


Noncovalent functionalization of multi-walled carbon nanotubes by pyrene containing polymers

Petar Petrov, Fabrice Stassin, Christophe Pagnouille and Robert Jérôme*

The surface modification of MWNTs by pyrene containing polymers is a very efficient method for making them dispersible in water, and in a variety of organic solvents and for preparing homogeneous nanocomposites.

2906

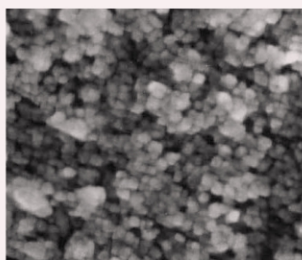


Light-emitting charge transfer species promoted by metal ion coordination

Massimo Boiocchi, Guido Colucci, Maurizio Licchelli,* Enrico Monzani and Donatella Sacchi

The coordinative interaction between zinc(II) and naphthalene-labeled diiminopyridine ligands induces the formation of light-emitting intracomplex charge transfer species: the complementary aromatic subunits on each ligand molecule are forced by the metal ion coordination geometry into a spatial arrangement extremely favourable to donor–acceptor interactions.

2908

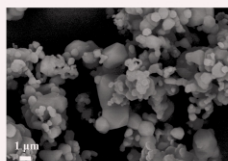


Photoelectrochemical decomposition of water on nanocrystalline BiVO₄ film electrodes under visible light

Kazuhiro Sayama,* Atsushi Nomura, Zhigang Zou, Ryu Abe, Yoshimoto Abe and Hironori Arakawa*

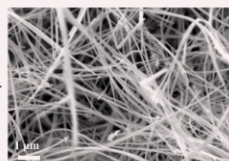
The nanocrystalline BiVO₄ film electrode on conducting glass showed an excellent efficiency (IPCE = 29% at 420 nm) for the decomposition of water under visible light.

2910



Hydrothermal treatment

NaAOT

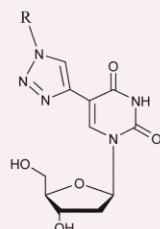
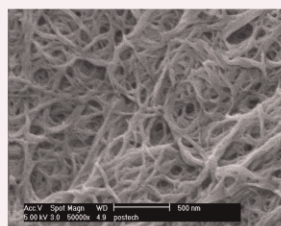


A self-seeded, surfactant-directed hydrothermal growth of single crystalline lithium manganese oxide nanobelts from the commercial bulky particles

Lizhi Zhang, Jimmy C. Yu,* An-Wu Xu, Quan Li, Kwan Wai Kwong and Ling Wu

A new method for converting commercial LiMn₂O₄ powders to crystalline nanobelts has been developed. This self-seeded, surfactant-directed hydrothermal growth process provides a unique strategy for the fabrication of one-dimensional nanomaterials.

2912

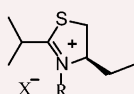


Novel low-molecular-weight hydrogelators based on 2'-deoxyuridine

Sun Min Park, Yoon Suk Lee and Byeang Hyeon Kim*

Novel nucleoside-based hydrogelators were designed and synthesized by simple base modification of 2-deoxyuridine.

2914



R= n-C₄H₉, n-C₁₂H₂₅
X⁻ = I, PF₆, BF₄, NTf₂

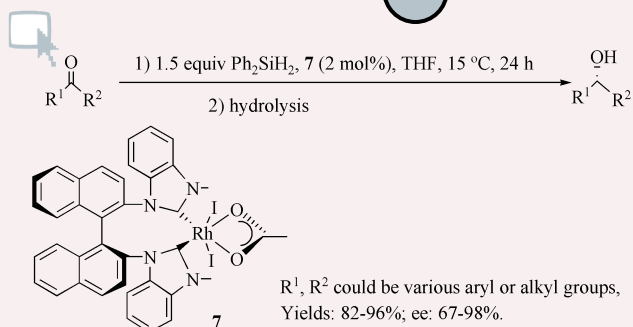
Chiral Ionic Liquids

Synthesis and properties of thiazoline based ionic liquids derived from the chiral pool

Jocelyne Levillain, Guillaume Dubant, Isabelle Abrunhosa, Mihaela Gulea and Annie-Claude Gaumont*

A novel class of enantiopure chiral ionic liquids based on amino alcohols is prepared in multi-gram scale. A preliminary example of chiral discrimination with racemic Mosher's acid salt is reported.

2916



Synthesis of novel axially chiral Rh–NHC complexes derived from BINAM and application in the enantioselective hydrosilylation of methyl ketones

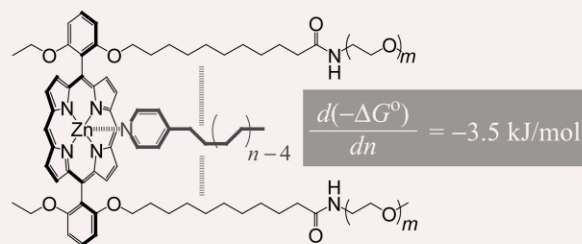
Wei-Liang Duan, Min Shi* and Guo-Bin Rong

Novel axially chiral Rh *N*-heterocyclic carbene complexes were prepared from axially dissymmetric 1,1'-binaphthalenyl-2,2'-diamine and applied in the Rh-catalyzed enantioselective hydrosilylation of methyl ketones. The corresponding *sec*-alcohols can be obtained in high yields with good to excellent ee.

2918

An efficient recognition motif for an alkyl moiety in water

Tadashi Mizutani,* Katsuyuki Kozake, Kenji Wada and Susumu Kitagawa



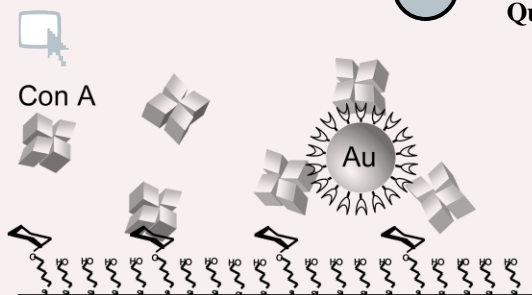
The artificial receptor showed the incremental binding free energy of 3.5 kJ mol⁻¹ per CH₂ for the recognition of an alkyl group in water.

2920

Quantitative analysis of multivalent interactions of carbohydrate-encapsulated gold nanoparticles with concanavalin A

Chun-Cheng Lin,* Yi-Chun Yeh, Chan-Yi Yang, Gee-Fong Chen, Yi-Chen Chen, Yi-Chun Wu* and Chia-Chun Chen*

Multivalent interactions between carbohydrate-encapsulated gold nanoparticles and Con A are found with high affinity and specificity.

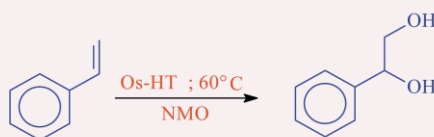


2922

The Os/Cu–Al-hydroxalate catalysed hydroxylation of alkenes

Holger B. Friedrich,* Mayashree Govender, Xolani Makhoba, T. Dennis Ngcobo and Martin O. Onani

A new Os/Cu–Al-hydroxalate-like catalyst is described which, with *N*-methylmorpholine oxide as co-oxidant, heterogeneously catalyses the hydroxylation of olefins to give diols selectively and in high yield.

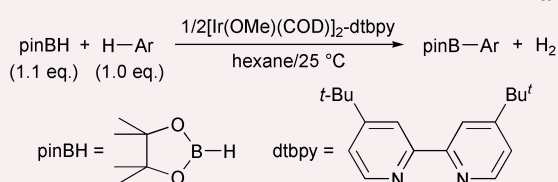


2924

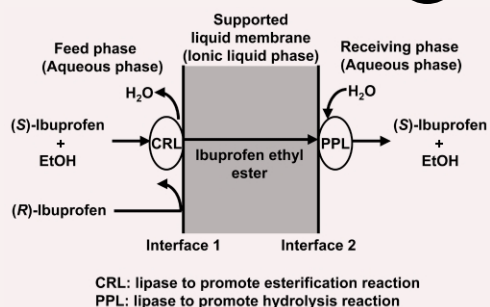
Room temperature borylation of arenes and heteroarenes using stoichiometric amounts of pinacolborane catalyzed by iridium complexes in an inert solvent

Tatsuo Ishiyama,* Yusuke Nobuta, John F. Hartwig and Norio Miyaura*

Aromatic C–H borylation of arenes and heteroarenes using stoichiometric amounts of pinacolborane was catalyzed by an iridium complex generated from 12[Ir(OMe)(COD)]₂ and 4,4'-di-*tert*-butyl-2,2'-bipyridine.



2926

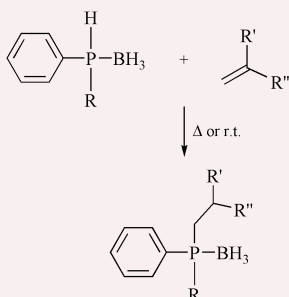


Enzyme-facilitated enantioselective transport of (*S*)-ibuprofen through a supported liquid membrane based on ionic liquids

Eijiro Miyako, Tatsuo Maruyama, Noriho Kamiya and Masahiro Goto*

From racemic ibuprofen, (*S*)-ibuprofen is selectively transported through a lipase-facilitated supported liquid membrane based on an ionic liquid.

2928

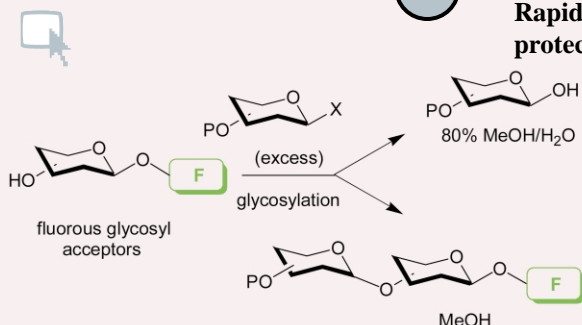


Regioselective uncatalysed hydrophosphination of alkenes: a facile route to *P*-alkylated phosphine derivatives

David Mimeau, Olivier Delacroix and Annie-Claude Gaumont*

The synthesis of alkylarylphosphines is easily carried out by hydrophosphination of unactivated alkenes under mild thermal activation; gram scale amounts of products can be prepared by this simple methodology.

2930

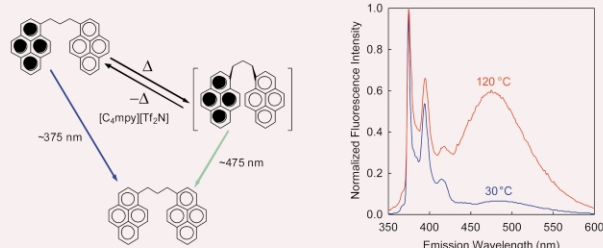


Rapid synthesis of oligosaccharides using an anomeric fluorosilyl protecting group

Leonardo Manzoni*

A fluorosilyl ether tag as protecting group at the anomeric position of sugar acceptors allows rapid synthesis of oligosaccharides by reducing the purification procedures to a simple and fast fluorosilyl solid-phase extraction.

2932



Noncontact two-color luminescence thermometry based on intramolecular luminophore cyclization within an ionic liquid

Gary A. Baker,* Sheila N. Baker and T. Mark McCleskey

A novel self-referencing luminescence thermometer based on reversible cyclization of a bis(1-pyrenyl) probe dissolved in a bis(triflyl)imide ionic liquid is reported.

2934

Design and synthesis of DNA-tethered ruthenium complexes that self-assemble into linear arrays

Kristen M. Stewart and Larry W. McLaughlin*

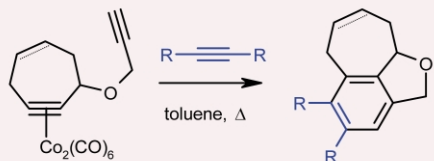


Ruthenium(II) bis(terpyridine) complexes have been prepared with two triethylene glycol tethering two identical 20-mer DNA sequences of uniform polarity. With the synthesis of a second complementary complex hybridization to form long linear arrays results.

2936

Tethered 2 + 2 + 2 cycloaddition reactions of cobalt–cycloheptyne complexes

Ahmed B. Mohamed and James R. Green*

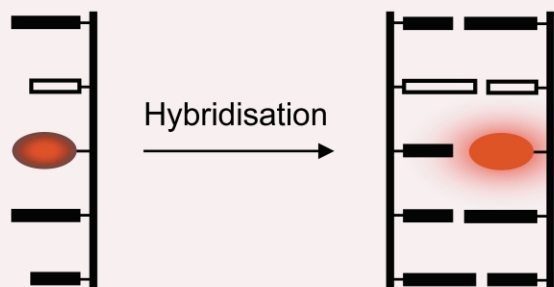


Cycloheptyne–dicobalt complexes substituted with a propargylic ether function undergo 2 + 2 + 2 cycloaddition reactions with an added alkyne. An all-intramolecular version of the 2 + 2 + 2 cycloaddition also has been developed.

2938

Thiazole orange as fluorescent universal base in peptide nucleic acids

Olaf Köhler and Oliver Seitz*

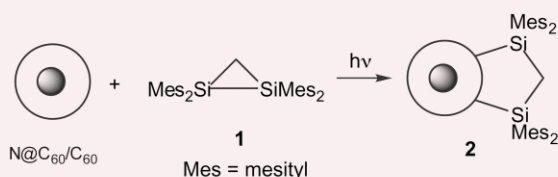


Thiazole orange has the characteristics of a universal PNA base that maintains duplex stability. Thiazole orange–PNA fluoresces upon hybridisation. Its emission properties allowed distinction between matched and single mismatched hybridisation.

2940

A comparison of the photochemical reactivity of N@C₆₀ and C₆₀: photolysis with disilirane

Takatsugu Wakahara, Yoichiro Matsunaga, Akira Katayama, Yutaka Maeda, Masahiro Kako, Takeshi Akasaka,* Mutsuo Okamura, Tatsuhisa Kato, Yoong-Kee Choe, Kaoru Kobayashi, Shigeru Nagase,* Houjin Huang and Masafumi Ata

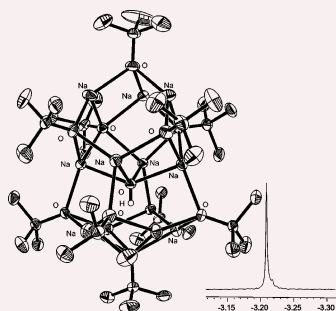


N@C₆₀ has a lower photochemical reactivity toward disilirane than C₆₀, although N@C₆₀ does not differ from C₆₀ in its thermal reactivity.

2942

Synthesis and structure of [Na₁₁(O^tBu)₁₀(OH)]: ¹H NMR shift of a hydroxide ion encapsulated in a 21-vertex alcoholate cage

Jens Geier and Hansjörg Grützmacher

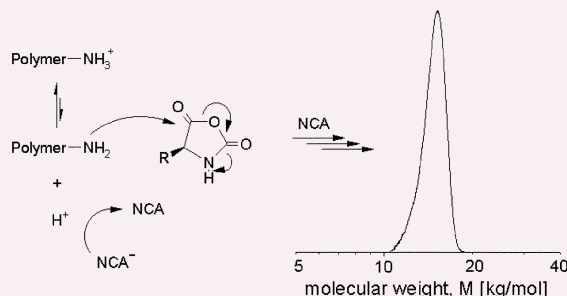


Stoichiometric addition of water to a solution of sodium tert.butanolate in hexane/TMEDA gives a 35% yield of crystalline material containing the title compound. The OH-proton encapsulated in this 21-vertex cage shows a ¹H NMR resonance at –3.21 ppm.

2944

Synthesis of nearly monodisperse polystyrene–polypeptide block copolymers via polymerisation of N-carboxyanhydrides

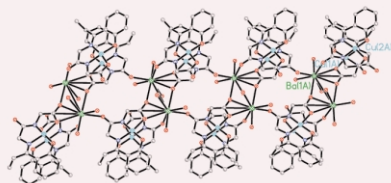
Ivaylo Dimitrov and Helmut Schlaad*



Primary amine hydrochlorides promote a well-controlled ring-opening polymerisation of Z-L-lysine-*N*-carboxyanhydride in DMF as the solvent at 40–80 °C. The polystyrene-*block*-poly(Z-L-lysine) copolymers synthesised exhibit a very narrow molecular weight distribution, close to a Poisson distribution.

COMMUNICATIONS

2946



A novel molecular ladder structure of Cu(II)–Ba(II) coordination polymer exhibiting ferromagnetic coupling

Yang Zou, Wenlong Liu, Song Gao, Jingli Xie and Qingjin Meng*

A novel one-dimensional ladder-like Cu–Ba compound $\{[\text{Ba}(\text{H}_2\text{O})_3(\text{CuL})_2] \cdot 2\text{H}_2\text{O}\}_n$ (H_3L = Glycylglycine, *N*-[1-(2-hydroxyphenyl)propylidene]), has been synthesized; it exhibits ferromagnetic interaction.

ADDITIONS AND CORRECTIONS

2948

Michael Harmata and Sumrit Wacharasindhu

Substitution of a bridgehead bromide by primary organolithium reagents

2948

Jeffrey M. Pietryga, Jamie N. Jones, Lucille A. Mullins, Robert J. Wiacek and Alan H. Cowley

An unprecedented mode of ligation for a bridged amidocyclopentadienide (constrained geometry) ligand; π -olefinic interactions with gallium and indium

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