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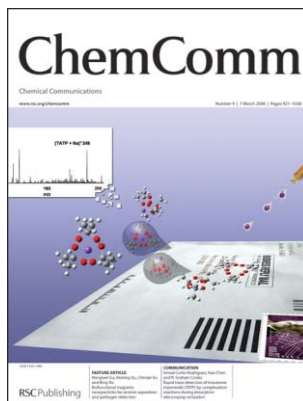
## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (9) 921-1036 (2006)



### Cover

See Christopher B. Smith *et al.*, page 950.  
Praseodymium ions induce a host-guest complex based on p-sulfonatocalix[4]arene to form helical strands, which assemble in parallel to generate a zeolite-like superhelical array. Image reproduced by permission of Christopher B. Smith, Leonard J. Barbour, Mohamed Makha, Colin L. Raston and Alexandre N. Sobolev from *Chem. Commun.*, 2006, 950.



### Inside cover

See Ismael Cotte-Rodríguez, Hao Chen and R. Graham Cooks, page 953.  
Reactant sodium ions sprayed onto the surface of an envelope contaminated with a trace amount of triacetone triperoxide (TATP) release the TATP into the air as stable complexes of  $m/z$  245 (TATP + Na)<sup>+</sup> and they are pulled into the mass spectrometer for analysis. Image reproduced by permission of Ismael Cotte-Rodríguez, Hao Chen and R. Graham Cooks from *Chem. Commun.*, 2006, 953.

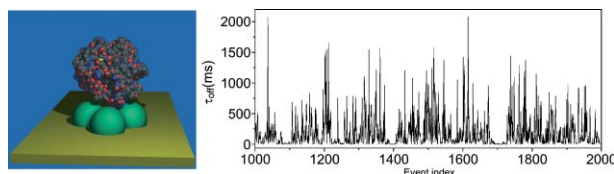
## 40TH ANNIVERSARY ARTICLE

935

### Do enzymes sleep and work?

Hans Engelkamp, Nikos S. Hatzakis, Johan Hofkens,\*  
Frans C. De Schryver, Roeland J. M. Nolte\* and  
Alan E. Rowan\*

Single-enzyme studies suggest that dynamic disorder is a general characteristic of enzyme catalysis.



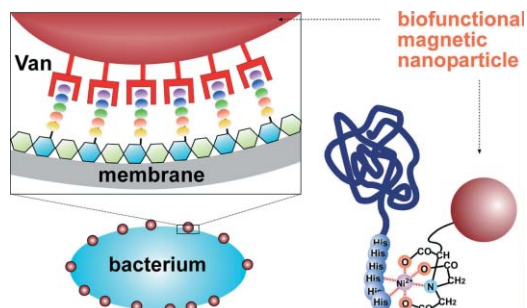
## FEATURE ARTICLE

941

### Biofunctional magnetic nanoparticles for protein separation and pathogen detection

Hongwei Gu, Keming Xu, Chenjie Xu and Bing Xu\*

This article highlights a general strategy to generate biofunctional magnetic nanoparticles that offers high sensitivity and high selectivity in protein separation and pathogen detection.



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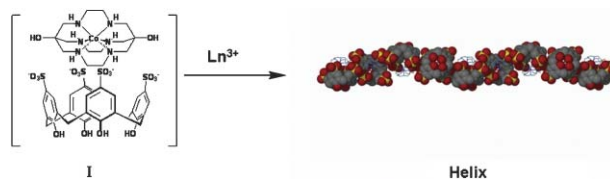
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**Lanthanide-induced helical arrays of  $\{Co(III)\}$  sepulchrate  $\cap$   $\{p$ -sulfonatocalix[4]arene $\}$  supermolecules**

Christopher B. Smith,\* Leonard J. Barbour, Mohamed Makha,\* Colin L. Raston\* and Alexandre N. Sobolev

The presence of lanthanide ( $Ln^{3+}$ ) ions induces the inclusion complex  $\{Co(diHOsar)\} \cap \{p$ -sulfonatocalix[4]arene $\}$  **I** to form a zeolite-like network comprised of parallel, single stranded helices.

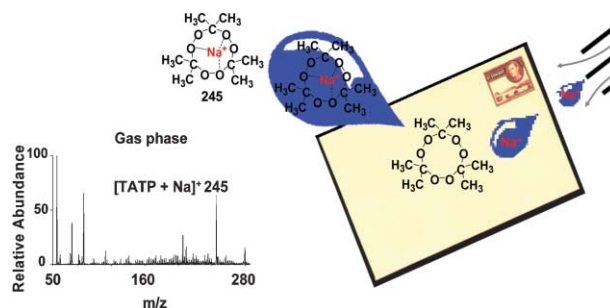


953

**Rapid trace detection of triacetone triperoxide (TATP) by complexation reactions during desorption electrospray ionization**

Ismael Cotte-Rodríguez, Hao Chen and R. Graham Cooks\*

The notorious explosive TATP is detected at low ng levels on ambient surfaces by complexation with alkali metals using a spray mass spectrometry technique which does not require any sample preparation and is highly specific.

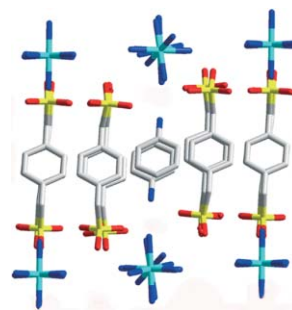


956

**Selective guest inclusion in a non-porous H-bonded host**

Sean A. Dalrymple and George K. H. Shimizu\*

A hydrogen-bonded host solid, based upon interactions between pillaring sulfonate groups and the second coordination sphere of hexamine metal ions, demonstrates reversible and selective guest inclusion, despite not having a porous interlayer.

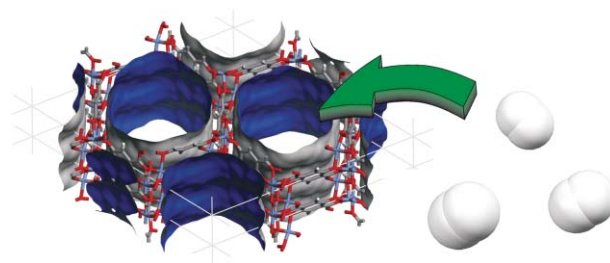


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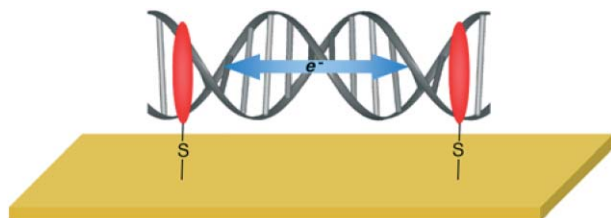
**Hydrogen adsorption in a nickel based coordination polymer with open metal sites in the cylindrical cavities of the desolvated framework**

Pascal D. C. Dietzel,\* Barbara Panella, Michael Hirscher, Richard Blom and Helmer Fjellvåg

The stable desolvated honeycomb-like framework of a nickel coordination polymer contains open-metal sites and can store up to 1.8 weight-% of hydrogen at 77 K in its one-dimensional channels of  $\sim 11 \times 11$  Å diameter.



962

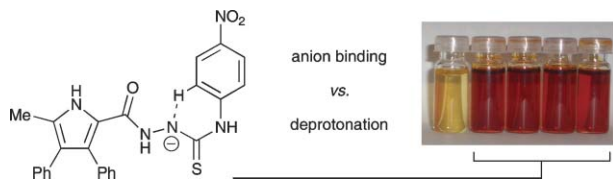


### An intercalator film as a DNA–electrode interface

Bradford J. Taft, Melissa A. Lapierre-Devlin and Shana O. Kelley\*

We report a novel DNA–electrode connectivity that provides strong electronic coupling. An intercalator film is described that binds DNA through stacking with the array of base pairs within the interior of the double helix. This type of electrode connection facilitates charge injection into DNA and promotes efficient electron transfer to redox active probes contained within the immobilized DNA film.

965

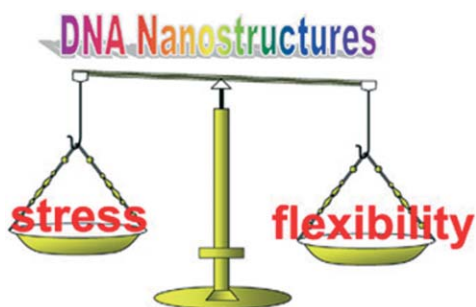


### Anion binding vs. deprotonation in colorimetric pyrrolylamidothiurea based anion sensors

Louise S. Evans, Philip A. Gale,\* Mark E. Light and Roberto Quesada\*

A pyrrolylamidothiurea deprotonates in the presence of *one* equivalent of *not only* fluoride, *but also* acetate, benzoate or dihydrogen phosphate in DMSO solution with structural studies using synchrotron radiation confirming thiourea deprotonation in the solid state.

968

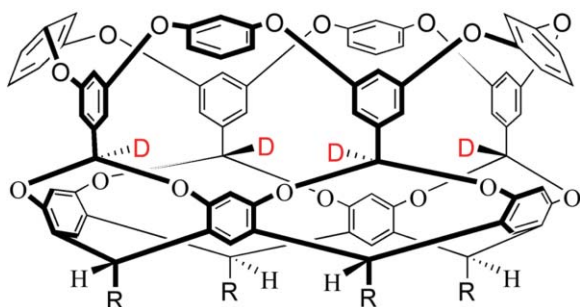


### Balancing flexibility and stress in DNA nanostructures

Yu He and Chengde Mao\*

A subtle balance of flexibility and stress is found to be critical for a DNA nanostructure to be a good self-assembly block.

970



### A deuterated deep-cavity cavitand confirms the importance of C–H⋯X–R hydrogen bonds in guest binding

Zachary R. Laughrey, Thomas G. Upton and Bruce C. Gibb\*

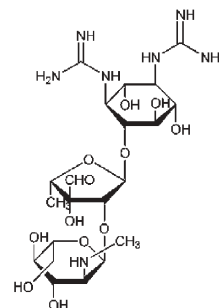
A deuterated cavitand host was examined for its affinity to a series of guests. For halogenated, preorganized guests binding was significantly stronger than the corresponding protium host.

973

### Use of streptomycin for precipitation and detection of proteinase K resistant prion protein (PrP<sup>Sc</sup>) in biological samples

Aly Moussa,\* Anthony W. Coleman, Anna Bencsik, Edwige Leclere, Florent Perret, Ambroise Martin and Hervé Perron

The ability of streptomycin to form multimolecular aggregates with pathogenic prion proteins and their recovery by precipitation *via* a low-speed centrifugation step has been demonstrated.

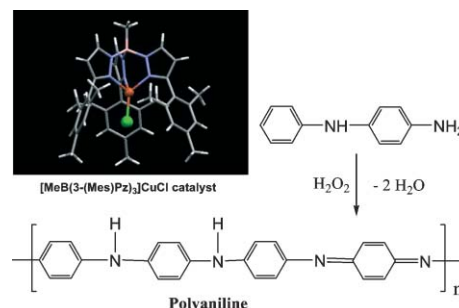


976

### A mild, copper catalyzed route to conducting polyaniline

H. V. Rasika Dias,\* Xiaoyu Wang, R. M. Gamini Rajapakse and Ronald L. Elsenbaumer

The aniline dimer has been polymerized cleanly under mild conditions to obtain polyaniline using a copper(II) scorpionate [MeB(3-(Mes)Pz)<sub>3</sub>]CuCl as the catalyst and H<sub>2</sub>O<sub>2</sub> as the oxidant.

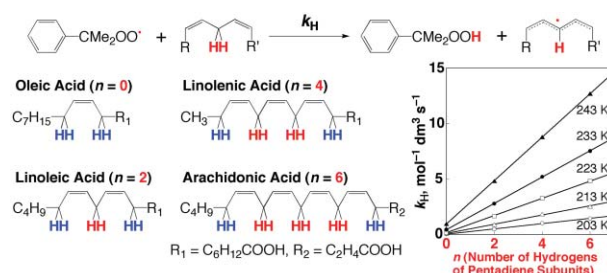


979

### Additivity rule holds in the hydrogen transfer reactivity of unsaturated fatty acids with a peroxy radical: mechanistic insight into lipoxygenase

Hironori Kitaguchi, Kei Ohkubo, Seiji Ogo and Shunichi Fukuzumi\*

A simple additivity rule holds in the hydrogen transfer reactivity of unsaturated fatty acids with cumylperoxy radical, which is expressed by the additive contributions of the reactivity of active hydrogens from the 1,4-pentadiene subunit and those of the allylic subunit.

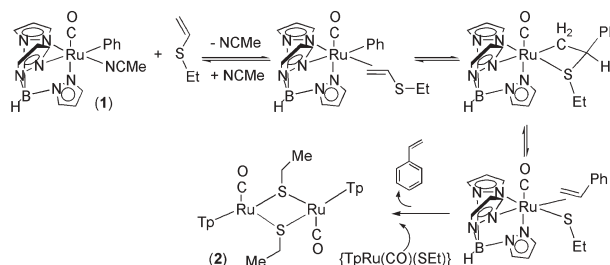


982

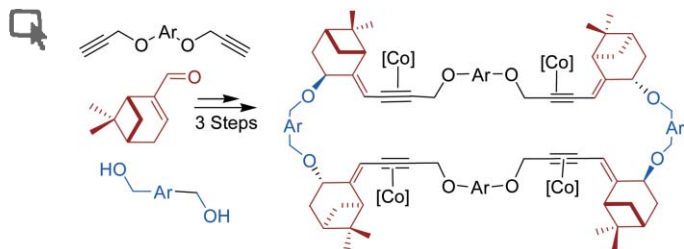
### Reactions of TpRu(CO)(NCMe)(Ph) with electron-rich olefins: examples of stoichiometric C–S, C–O and C–H bond cleavage

Laurel A. Goj, Marty Lail, Karl A. Pittard, Kimberly C. Riley, T. Brent Gunnoe\* and Jeffrey L. Petersen

The Ru<sup>II</sup> complex TpRu(CO)(NCMe)(Ph) reacts with the electron-rich olefins ethyl vinyl sulfide and 2,3-dihydrofuran to initiate unusual C–S, C–H and C–O bond cleavage reactions.



985

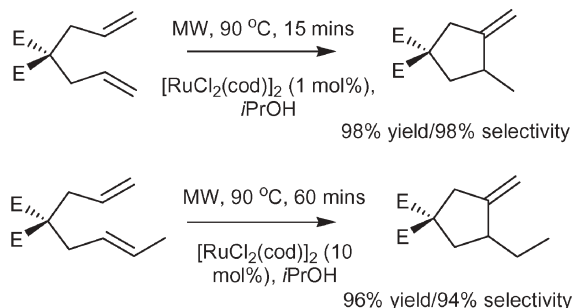


### Synthesis of polymetallic macrocyclic terpene-derived hybrids

Elsa Álvaro, María C. de la Torre\* and Miguel A. Sierra\*

Terpene alkyne systems act as templates in the preparation of natural product hybrids and in macrocyclic structures having up to four terpene units and eight Co-atoms, which are built by using the Nicholas reaction

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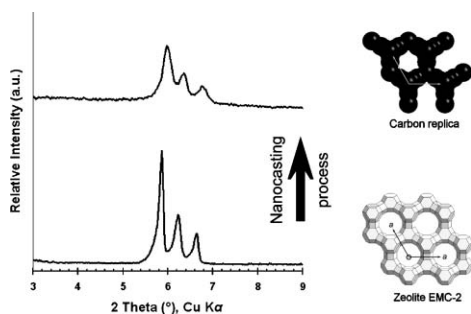


### Ruthenium(II)-catalysed cycloisomerisation of 1,6-dienes by focused microwave dielectric heating: improved rates and selectivities leading to *exo*-methylenecyclopentanes

Ian J. S. Fairlamb,\* Gerard P. McGlacken and Felix Weissberger

Microwave dielectric heating in Ru-catalysed cycloisomerisation of 1,6-dienes. Substantially improved reaction rates are attained for a series of 1,6-diene substrates, with equivalent or higher isomeric purity than conventional thermal heating.

991

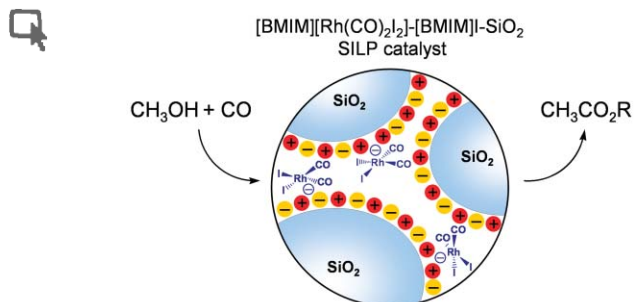


### First zeolite carbon replica with a well resolved X-ray diffraction pattern

Fabrice O. M. Gaslain, Julien Parmentier,\* Valentin P. Valtchev and Joël Patarin

The present study demonstrates that for the nanocasting process with zeolites, a careful choice of the zeolite structure type (EMT) allows the formation of faithful carbon replica exhibiting up to three well resolved XRD peaks.

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### First application of supported ionic liquid phase (SILP) catalysis for continuous methanol carbonylation

Anders Riisager,\* Betina Jørgensen, Peter Wasserscheid and Rasmus Fehrmann

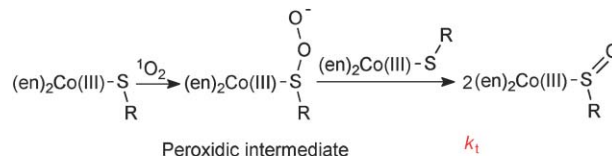
A solid, silica-supported ionic liquid phase rhodium iodide Monsanto-type catalyst system, [BMIM][Rh(CO)<sub>2</sub>I]-[BMIM]I-SiO<sub>2</sub>, exhibits excellent activity and selectivity towards acetyl products in fixed-bed, continuous gas-phase methanol carbonylation.

997

### Photooxidation of Co-thiolato complexes in protic and aprotic solvents

Billy Hernandez, Yanju Wang, Dong Zhang and Matthias Selke\*

Protic solvents decrease the susceptibility of the thiolate ligand in Co(III) thiolato complexes toward attack by singlet oxygen, but greatly increase the conversion of the peroxidic intermediate to the sulfenato product.



$k_1$  = rate constant of  $^1\text{O}_2$  removal,  $k_1(\text{water}) < k_1(\text{MeOH}) < k_1(\text{DMF})$

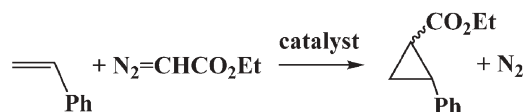
$k_r$  = rate of product formation,  $k_r(\text{water}) > k_r(\text{MeOH}) > k_r(\text{DMF})$

1000

### A non-fluorous copper catalyst for the styrene cyclopropanation reaction in a fluorous medium

Juan Urbano, Rocio Izarra, Jose Luis Gómez-Ariza, Swiatoslaw Trofimenko, M. Mar Díaz-Requejo\* and Pedro J. Pérez\*

The complex  $\text{Tp}^{\text{Br}3}\text{Cu}(\text{NCMe})$ , containing no fluorine atoms, can be dissolved in the perfluoropolyether FOMBLIN<sup>®</sup> and employed as a catalyst for the styrene cyclopropanation reaction with ethyl diazoacetate, with activities and diastereoselectivities identical to those observed under homogeneous conditions.



catalyst =  $\text{Tp}^{\text{Br}3}\text{Cu}(\text{NCMe})$  in FOMBLIN  
five recycles with constant 90% yield and cis:trans 60:40

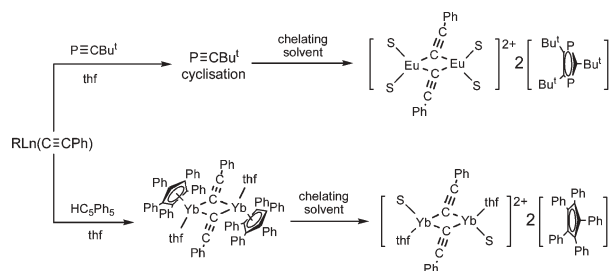
FOMBLIN:  $\text{CF}_3\text{O}[-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-]_x(-\text{CF}_2\text{O}-)_y\text{CF}_3$

1003

### Dinuclear alkynyllanthanoid(II) dications with pentaphenylcyclopentadienyl or tri-tert-butylphosphacyclopentadienyl counter ions

Craig M. Forsyth, Glen B. Deacon,\* Leslie D. Field, Cameron Jones, Peter C. Junk, Danielle L. Kay, Anthony F. Masters and Anne F. Richards

Displacement of bulky 1,3- $\text{P}_2\text{Bu}^t_3$  or  $\text{C}_5\text{Ph}_5$  ligands from lanthanoid(II) centres, simply by addition of a chelating donor, enables stabilisation of novel cationic organolanthanoid(II) species having a residual alkynyllanthanoid moiety.

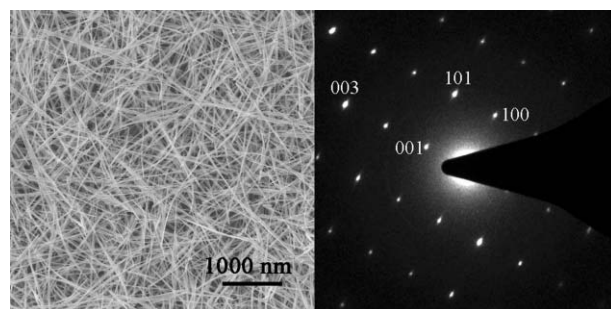


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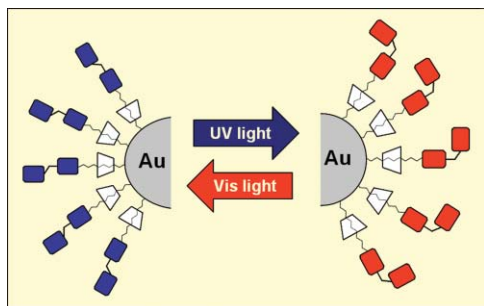
### High-yield synthesis of selenium nanowires in water at room temperature

Qing Li and Vivian Wing-Wah Yam\*

High-quality t-Se nanowires were obtained in high yield *via* a facile and environmentally benign route in water at room temperature using ascorbic acid as the reducing agent under the assistance of  $\beta$ -cyclodextrin, and HRTEM characterization demonstrated that the nanowires were structurally uniform single crystals with a growth direction of [001].



1009

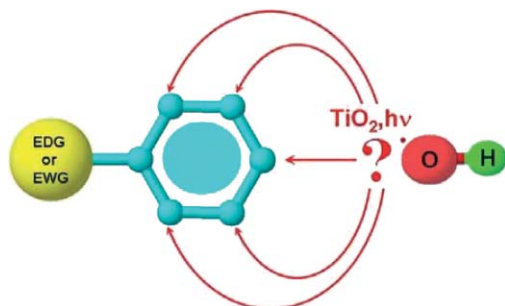


### Highly photoresponsive monolayer-protected gold clusters by self-assembly of a cyclodextrin–azobenzene-derived supramolecular complex

Fiorella Callari, Salvatore Petralia and Salvatore Sortino\*

Reversibly-photoswitchable gold nanoparticles containing azobenzene and exhibiting a light response “virtually identical” to that of the free chromophore were achieved by self-assembling a host–guest inclusion complex between  $\alpha$ -cyclodextrin and an azobenzene-terminated alkanethiol in an aqueous medium.

1012

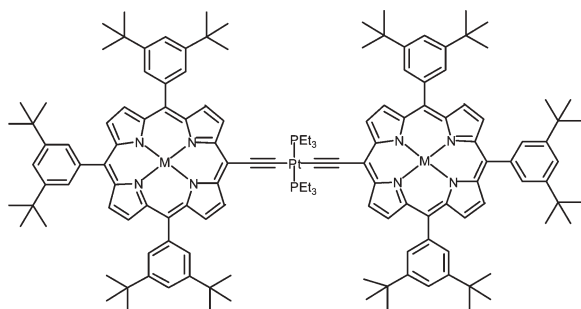


### Influence of the substituent on selective photocatalytic oxidation of aromatic compounds in aqueous $\text{TiO}_2$ suspensions

Giovanni Palmisano,\* Maurizio Addamo, Vincenzo Augugliaro, Tullio Caronna, Elisa García-López, Vittorio Loddo and Leonardo Palmisano

Experimental results are reported showing selectivity/unselectivity of hydroxyl radical in the photocatalytic oxidation of substituted aromatic compounds.

1015

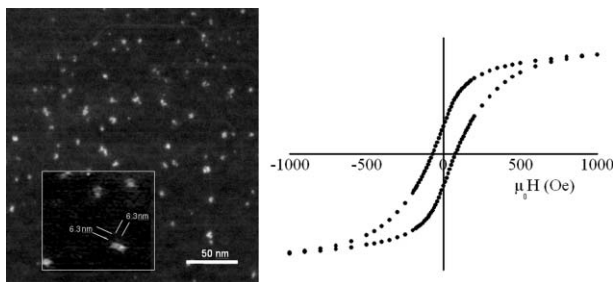


### Porphyrin dimers bridged by a platinum–diacetylide unit

Yi-Jen Chen, Szu-Shuo Chen, Shang-Shih Lo, Teng-Hui Huang, Chen-Chang Wu, Gene-Hsiang Lee, Shie-Ming Peng and Chen-Yu Yeh\*

Novel platinum diacetylide-bridged porphyrin dimers have been synthesized and the dinickel complex exhibits interporphyrin electronic communication.

1018



### Superparamagnetic bimetallic cyanide-bridged coordination nanoparticles with $T_B = 9$ K

Laure Catala,\* Alexandre Gloter, Odile Stephan, Guillaume Rogez and Talal Mallah\*

Dispersible, nearly isolated 6 nm nanoparticles of the  $\text{CsNiCr}(\text{CN})_6$  Prussian blue analogue coated with polyvinylpyrrolidone (PVP) show superparamagnetic behaviour with a relatively high blocking temperature  $T_B = 9$  K.

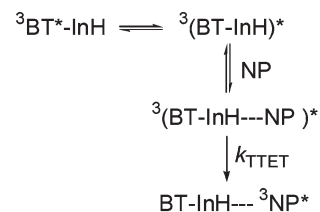


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### Triplet exciplexes as energy transfer photosensitisers

Julia Pérez-Prieto,\* Raquel E. Galian,  
 María C. Morant-Miñana and Miguel A. Miranda

Triplet–triplet energy transfer occurs from BT–InH exciplexes, to NP derivatives with remarkable stereodifferentiation.



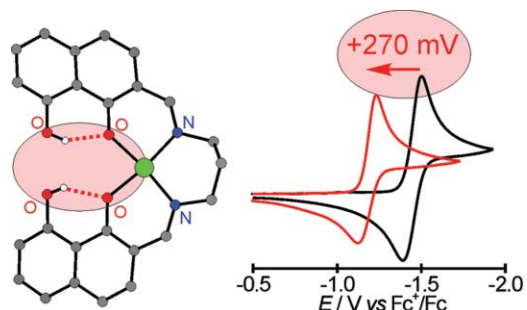
BT, InH and NP = Chiral benzoylthiophene, indole and naphthalene derivatives.

1024

### Direct influence of hydrogen-bonding on the reduction potential of a Cu<sup>II</sup> center

Thorsten Glaser,\* Ioannis Liratzis, Olga Kataeva,  
 Roland Fröhlich, Manuel Piacenza and Stefan Grimme

A positive shift of 270 mV in the reduction potential  $E^0$  of Cu<sup>II</sup> to Cu<sup>I</sup> arises from the presence of two OH groups in the second coordination sphere of the copper ion. DFT calculations support the conception that this destabilization of the Cu<sup>II</sup> oxidation state is due to hydrogen-bonding of the neighboring OH groups to the coordinated aryloxide donors.

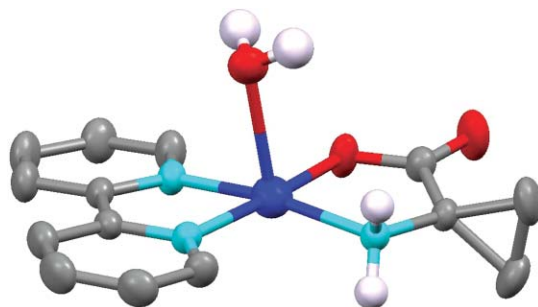


1027

### ACC-Oxidase like activity of a copper (II)–ACC complex in the presence of hydrogen peroxide. Detection of a reaction intermediate at low temperature

Wadih Ghattas, Christian Gaudin, Michel Giorgi,  
 Antal Rockenbauer, A. Jalila Simaan\* and Marius Réglier

The [(Bpy)Cu(ACC)(H<sub>2</sub>O)]·ClO<sub>4</sub> complex was prepared and treated with hydrogen peroxide, and ethylene production in an ACC-Oxidase like activity was observed. A brown species that could be a key intermediate in the reaction was detected at low temperature.

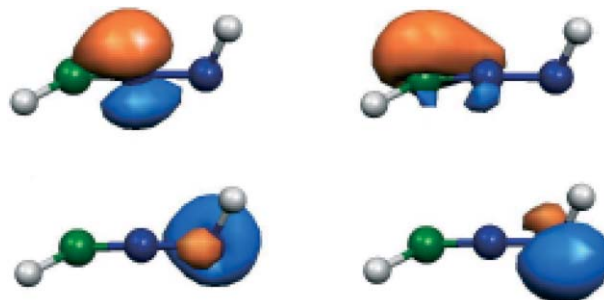


1030

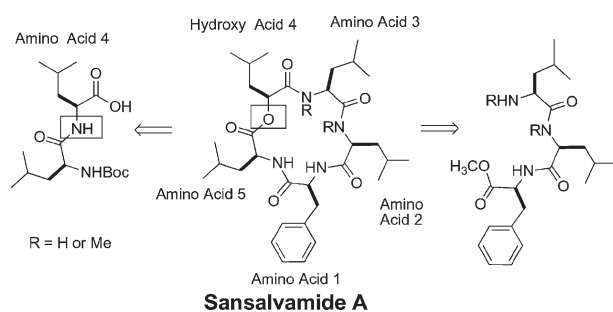
### The electronic structure of nitrilimine: absence of the carbenic form

Fausto Cargnoni, Giorgio Molteni, David L. Cooper,  
 Mario Raimondi and Alessandro Ponti\*

The electronic structure of nitrilimine HCNNH is shown to essentially be propargylic, with little, if any, contribution from the carbenic resonance form.



1033



### Synthesis and novel structure–activity relationships of potent sansalvamide A derivatives

Katerina Otrubova, Thomas J. Styers, Po-Shen Pan, Rodrigo Rodriguez, Kathleen L. McGuire\* and Shelli R. McAlpine\*

The synthesis of twelve Sansalvamide A (San A) derivatives produced four compounds that exhibited potency comparable to that of a current drug on the market. In addition, described is the discovery of a key structure–activity relationship (SAR).

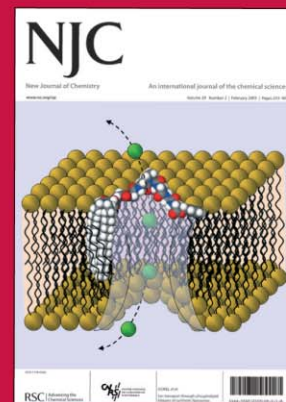
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