

# ChemComm

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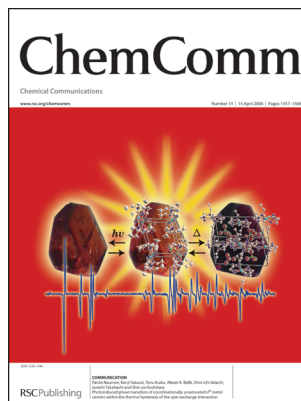
## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (14) 1457-1568 (2006)



### Cover

See Mohamed Eddaoudi *et al.*, page 1488.  
Zeolites go organic: A fragment of the *rho*-ZMOF - yellow spheres represent the largest (18.2 Å) that would fit in the *a*-cavities. Background: *rho*-ZMOF crystals, as-synthesized transparent and red after Acridine Orange exchange. Image reproduced by permission of Yunling Liu, Victor Ch. Kravtsov, Randy Larsen and Mohamed Eddaoudi from *Chem. Commun.*, 2006, 1488.



### Inside cover

See Panče Naumov *et al.*, page 1491.  
Phase switching of coordinationally unsaturated pseudo-Jahn-Teller centers within the hysteresis region of the low-temperature phase transition is triggered by photoexcitation. Image reproduced by permission of Panče Naumov, Kenji Sakurai, Toru Asaka, Alexei A. Belik, Shin-ichi Adachi, Junichi Takahashi and Shin-ya Koshihara from *Chem. Commun.*, 2006, 1491.

## CHEMICAL TECHNOLOGY

T13

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

## Chemical Technology

April 2006/Volume 3/Issue 4

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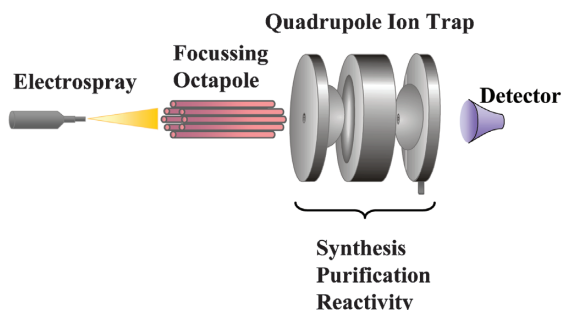
## FEATURE ARTICLE

1469

### The 3D quadrupole ion trap mass spectrometer as a complete chemical laboratory for fundamental gas-phase studies of metal mediated chemistry

Richard A. J. O'Hair\*

The use of the multistage mass spectrometry capabilities of the quadrupole ion trap mass spectrometer to examine metal mediated chemistry relevant to catalysis, C-C bond coupling, bioinorganic and supramolecular chemistry is highlighted.



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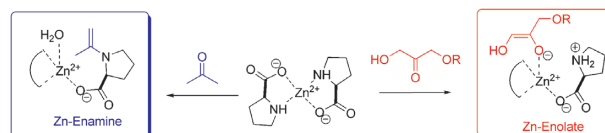
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1482

### Dual mechanism of zinc-proline catalyzed aldol reactions in water

Jacob Kofoed, Tamis Darbre and Jean-Louis Reymond\*

The aqueous aldolization catalyzed by zinc-proline and secondary amines occurs *via* an enamine with acetone and *via* an enolate with dihydroxyacetone, as shown by reductive trapping and Brønsted coefficient studies.

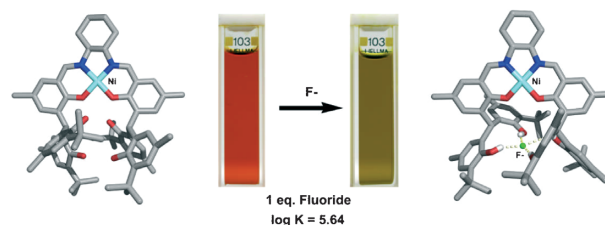


1485

### Metal salen complexes incorporating triphenoxymethanes: efficient, size selective anion binding by phenolic donors with a visual report

Eric R. Libra and Michael J. Scott\*

A metal salen complex has been designed to orientate four phenol groups into a tetrahedral array that tightly binds fluoride ion through four OH...F hydrogen bonding interactions.

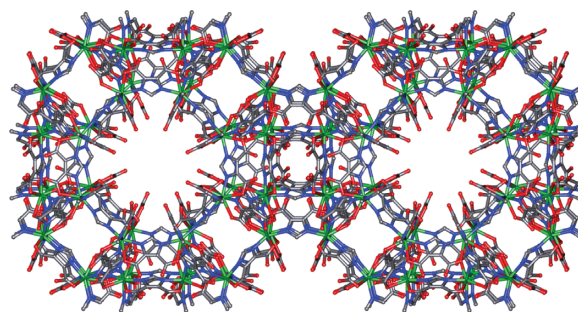


1488

### Molecular building blocks approach to the assembly of zeolite-like metal-organic frameworks (ZMOFs) with extra-large cavities

Yunling Liu, Victor Ch. Kravtsov, Randy Larsen and Mohamed Eddaoudi\*

Two novel porous anionic zeolite-like metal-organic frameworks, *rho*-ZMOF and *sod*-ZMOF, have been synthesized by metal-ligand-directed assembly of rigid and directional tetrahedral building units,  $\text{InN}_4$  synthesized *in-situ*, and doubly deprotonated imidazolecarboxylic acid ligands.

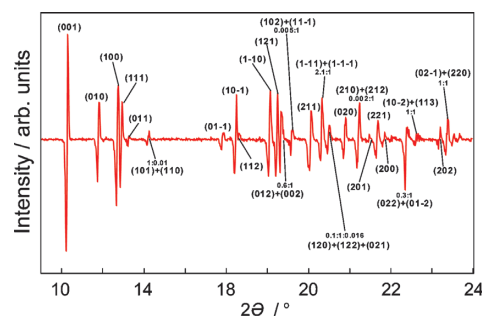


1491

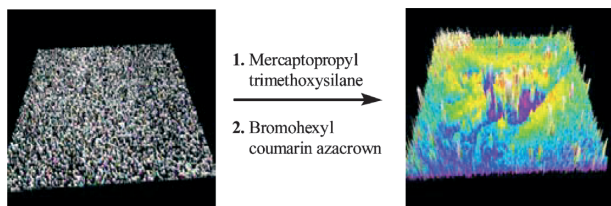
### Photoinduced phase transition of coordinationally unsaturated $d^9$ metal centers within the thermal hysteresis of the spin exchange interaction

Panče Naumov,\* Kenji Sakurai, Toru Asaka, Alexei A. Belik, Shin-ichi Adachi, Junichi Takahashi and Shin-ya Koshihara

Coordinationally unsaturated  $d^9$  pseudo-Jahn-Teller centers can be switched between two phases by LMCT-photoexcitation within the hysteresis region of the ferromagnetic-to-antiferromagnetic phase transition.



1494

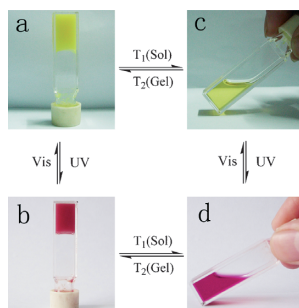


### Spectroscopic detection of Saxitoxin: an alternative to mouse bioassay

Péter Kele, Jhony Orbulescu, Robert E. Gawley and Roger M. Leblanc\*

We report the surface modification of quartz with a coumarin-aza-crown derivative. Fluorescence enhancement allowed the detection of Saxitoxin within one order of magnitude of the mouse bioassay which is the current benchmark for Saxitoxin detection.

1497

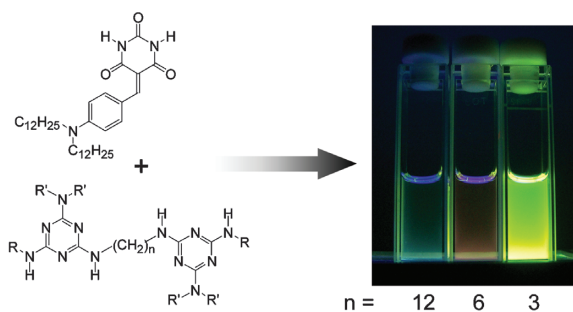


### A multiple switching bisthienylethene and its photochromic fluorescent organogelator

Sheng Wang, Wei Shen, Yanli Feng and He Tian\*

A fluorescent photochromic bisthienylethene bridged naphthalimide bearing cholesteryl groups was synthesized and it showed multi-switching behaviour in solution by light, thermal, fluoride ions and proton stimulation and obvious photochromic process in gel phase.

1500

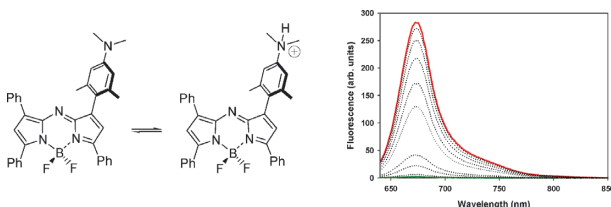


### Tunable interchromophore electronic interaction of a merocyanine dye in hydrogen-bonded supramolecular assemblies scaffolded by bismelamine receptors

Shiki Yagai,\* Masatsugu Higashi, Takashi Karatsu and Akihide Kitamura\*

The absorption and fluorescence properties of a barbiturate-type donor- $\pi$ -acceptor (D- $\pi$ -A) merocyanine dye are controlled by complexation with dimeric melamine receptors featuring different tether lengths.

1503



### Impact of a conformationally restricted receptor on the $\text{BF}_2$ chelated azadipyromethene fluorosensing platform

John Killoran and Donal F. O'Shea\*

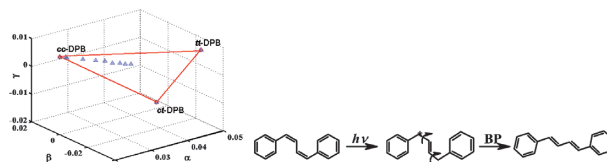
A flexible modular synthesis of a new class of visible red fluorosensors based upon either an integrated or virtual spacer design is reported. Sensor performance reveals large off-on fluorescence intensity responses to acid analyte with a low response to microenvironment polarity.

1506

### Photoisomerization of *cis,cis*-1,4-diphenyl-1,3-butadiene in glassy media at 77 K: the bicycle-pedal mechanism

Jack Saltiel,\* Tallapragada S. R. Krishna, Andrzej M. Turek and Ronald J. Clark

The *cis-trans* photoisomerization of *cis,cis*-1,4-diphenyl-1,3-butadiene in a soft isopentane glass at 77 K gives significant two-bond photoisomerization in contrast to fluid solution and hard glassy media where only one-bond isomerizes.

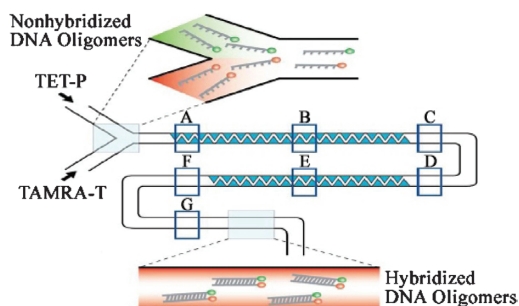


1509

### Fast and sensitive analysis of DNA hybridization in a PDMS micro-fluidic channel using fluorescence resonance energy transfer

Kwon-hae Yea, Sangyeop Lee, Jaebum Choo,\* Chil-Hwan Oh and Sanghoon Lee

This research applies fluorescence resonance energy transfer (FRET) to detect DNA hybridization reactions in a PDMS microfluidic channel. This technique overcomes many of the drawbacks of microarray chips, such as the long hybridization time and inconvenient immobilization procedures.

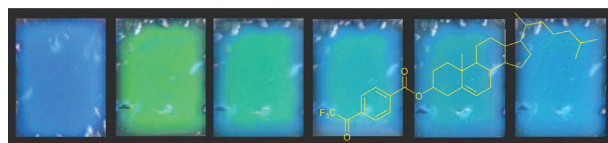


1512

### Functional liquid crystal films selectively recognize amine vapours and simultaneously change their colour

Nicole Kirchner, Linda Zedler, Thomas G. Mayerhöfer and Gerhard J. Mohr\*

A liquid crystal film containing a selective cholesteric receptor molecule shows reversible colour changes from blue to green upon exposure to gaseous aliphatic amines.

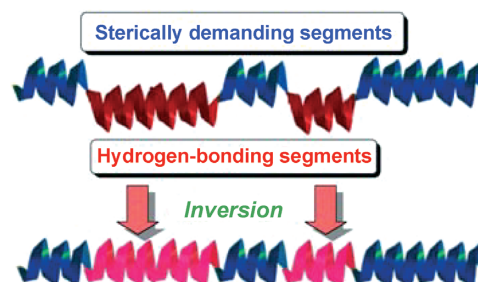


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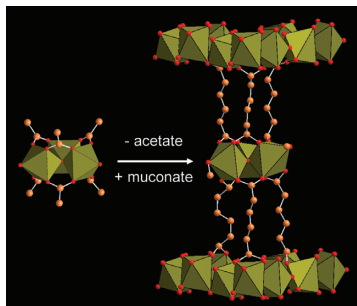
### Chiroptical inversion induced by sandwiching units in chiral polythiourethane

Atsushi Nagai, Bungo Ochiai and Takeshi Endo\*

Chiroptical behavior of a hydrogen-bond-regulated chiral polythiourethane segment was induced by sandwiching sterically demanding segments in a copolymer prepared by cationic ring-opening copolymerization of chiral cyclic thiourethanes derived from L-serine.



1518

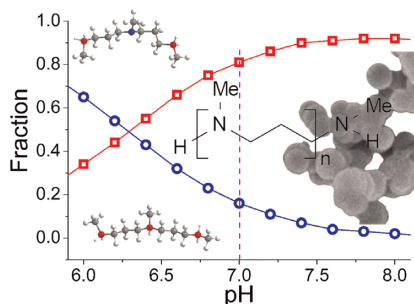


### An EXAFS study of the formation of a nanoporous metal–organic framework: evidence for the retention of secondary building units during synthesis

Suzy Surblé, Franck Millange, Christian Serre, Gérard Férey and Richard I. Walton\*

Trimeric iron oxide clusters are found in intermediate amorphous phases and in the synthesis solution of nanoporous MIL-89, proving that they can be considered as true secondary building units of the extended network.

1521

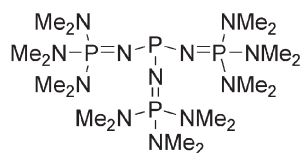


### A new stepwise synthesis of a family of propylamines derived from diatom silaffins and their activity in silicification

Vadim V. Annenkov,\* Siddharth V. Patwardhan, David Belton, Elena N. Danilovtseva and Carole C. Perry\*

A new method for the stepwise synthesis of propylamines as found in diatoms is presented and their activity in silicic acid condensation is described.

1524

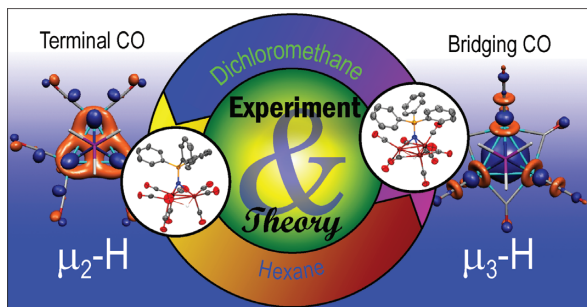


### High basicity of phosphorus–proton affinity of tris-(tetramethylguanidinyl)phosphine and tris-(hexamethyltriaminophosphazeny)phosphine by DFT calculations

Borislav Kovačević\* and Zvonimir B. Maksić

It is predicted by DFT calculations that tris-(hexamethyltriaminophosphazeny)phosphine should exhibit extremely high basicity ( $pK_a(\text{MeCN}) = 50 \pm 1$  units).

1527



### Experimental and computational studies on the solvent-controlled cluster isomerism of $\text{Ru}_3(\text{H})(\text{CO})_9(\text{NPPH}_3)$ and related dynamics

Roberto Pattacini, Giovanni Predieri, Antonio Tiripicchio,\* Carlo Mealli\* and Andrew D. Phillips

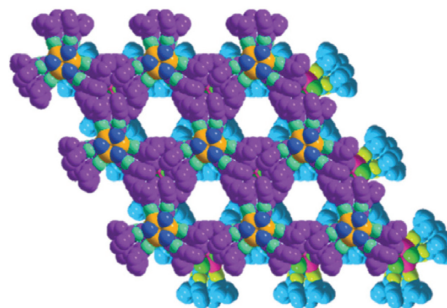
Two isomers of  $\text{Ru}_3(\text{H})(\mu_3\text{-NPPH}_3)(\text{CO})_9$  are described through a combined experimental and theoretical study, which highlights key intermediates for their formation and a solvent dependent interconversion.

1530

 **Porous material for absorption and luminescent detection of aromatic molecules in water**

Yan Bai, Guang-jie He, Yong-gang Zhao, Chun-ying Duan,\* Dong-bin Dang and Qing-jin Meng\*

A two-dimensional porous framework, which was formed from neutral discrete hexanuclear copper clusters *via* self-assembly, exhibited highly selective absorption of aromatic molecules in water with special fluorescent response.

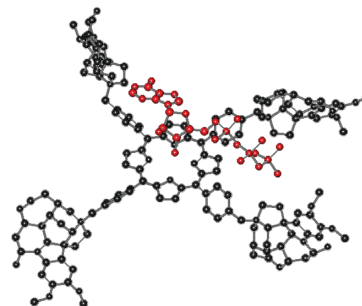


1533

**Optical sensing system for ATP using porphyrin–alkaloid conjugates**

Zdeněk Kejík, Kamil Záruba, David Michalík, Jiří Šebek, Juraj Dian, Stasis Pataridis, Karel Volka and Vladimír Král\*

Tetrabrucin–porphyrin conjugate as a sensor for ATP was designed and tested; selectivity for ATP was proved in the presence of ADP and AMP.

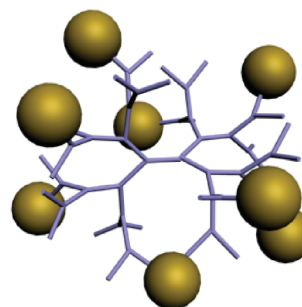


1536


**A nanoparticle–dendrimer conjugate prepared from a one-step chemical coupling of monofunctional nanoparticles with a dendrimer**

James G. Worden, Qiu Dai and Qun Huo\*

A nanoparticle–dendrimer conjugate with multiple nanoparticles attached to a single dendrimer was prepared by a one-step amide coupling reaction between monofunctional gold nanoparticles and a PAMAM dendrimer.

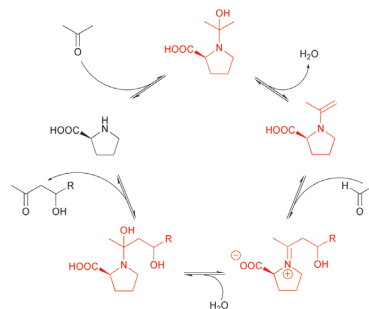


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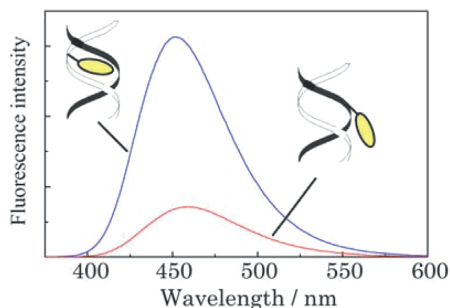
 **ESI-MS study on the aldol reaction catalyzed by L-proline**

Cesar Marquez and Jürgen O. Metzger\*

ESI-MS study of the organocatalytic aldol reaction catalyzed by L-proline has allowed detection and characterization of all the intermediates (given in red) assumed for the catalytic cycle.



1542

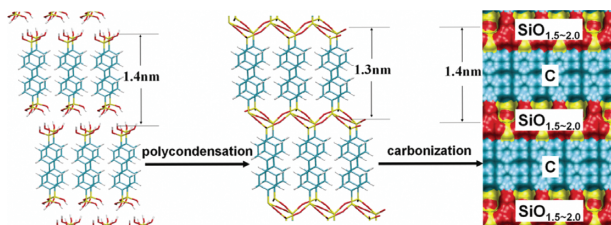


### Probing the microenvironments in the grooves of Z-DNA using dan-modified oligonucleotides

Takumi Kimura, Kiyohiko Kawai and Tetsuro Majima\*

The environment-sensitive fluorophore dan (6-dimethylamino-2-acyl-naphthalene)-modified dC or dG bases were introduced into the Z-DNA forming sequence. It was demonstrated that both grooves of Z-DNA are more hydrated than those of B-DNA.

1545

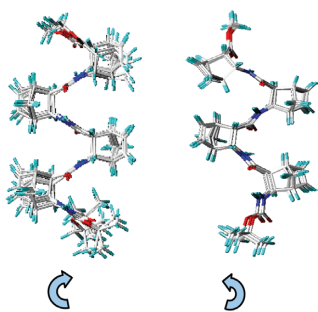


### Mesoscopically ordered organosilica and carbon-silica hybrids with uniform morphology by surfactant-assisted self-assembly of organo bis-silanetriols

Jiebin Pang, Lu Yang, Douglas A. Loy, Huisheng Peng, Henry S. Ashbaugh, Joel Mague, C. Jeffrey Brinker and Yunfeng Lu\*

Organosilica and carbon-silica hybrids with long-range molecular ordering and uniform particle morphology have been synthesized by thermal polycondensation and carbonization of self-assembled organo bis-silanetriols.

1548

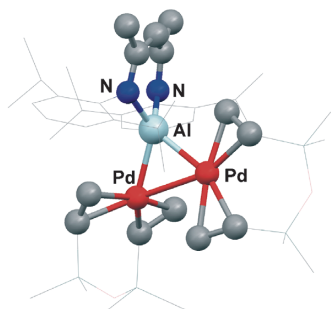


### Oligomers of *cis*- $\beta$ -norbornene amino acid: Formation of $\beta$ -strand mimetics

Srivari Chandrasekhar,\* Bathini Nagendra Babu, Anabathula Prabhakar, Ambadi Sudhakar, Marepally Srinivasa Reddy, Marelli Udaya Kiran and Bharatam Jagadeesh\*

The oligomers of constrained *cis*- $\beta$ -norbornene amino acid were synthesised and characterised by NMR, CD, IR and MD. The results showed the formation of both right and left handed consecutive 6-membered hydrogen-bonded strands for [2*S*,3*R*] and [2*R*,3*S*] enantiomers, respectively.

1551



### The Al(I) bisimidinate Al(DDP) as a metalloid NHC type ligand for Pd(0) complexes and clusters

Andreas Kempter, Christian Gemel and Roland A. Fischer\*

Two clusters with a Pd<sub>2</sub> core and the Al(I) bisimidinate Al(DDP) as a bridging ligand have been investigated, suggesting a strong similarity of the coordination properties of Al(DDP) to the isolobal NHC ligands.

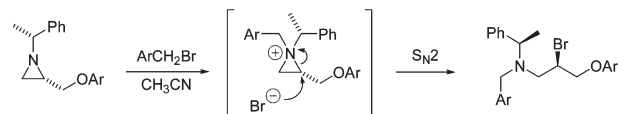


1554

### Regio- and stereospecific ring opening of 1,1-dialkyl-2-(aryloxymethyl)aziridinium salts by bromide

Matthias D'hooghe, Veronique Van Speybroeck, Michel Waroquier and Norbert De Kimpe\*

Enantiomerically pure 2-(aryloxymethyl)aziridines are efficiently transformed into chiral *N*-(2-bromo-3-aryloxypropyl)amines *via* intermediate aziridinium salts and the experimental results are rationalized on the basis of high level *ab initio* calculations.

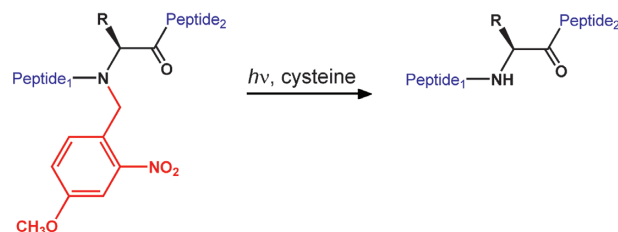


1557

### Synthesis, stability and optimized photolytic cleavage of 4-methoxy-2-nitrobenzyl backbone-protected peptides

Erik C. B. Johnson and Stephen B. H. Kent\*

We demonstrate the potential of 4-methoxy-2-nitrobenzyl as a Boc chemistry-compatible fully reversible backbone modification for synthetic peptides.

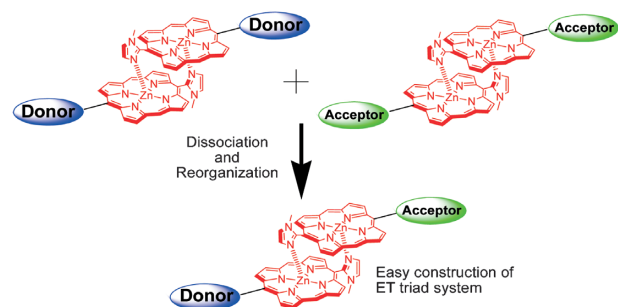


1560

### A supramolecular photosynthetic triad of slipped cofacial porphyrin dimer, ferrocene, and fullerene

Hirokichi Nakagawa, Kazuya Ogawa, Akiharu Satake and Yoshiaki Kobuke\*

A supramolecular triad consisting of self-assembled imidazolyl-zinc-porphyrin dimer, ferrocene, and fullerene was successfully constructed, resulting in long-lived charge separated species after efficient photoinduced electron transfer and charge shift reactions.

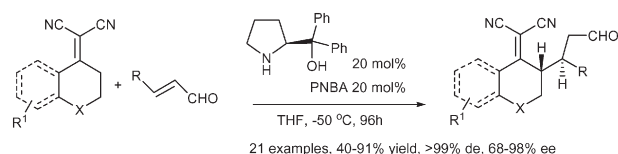


1563

### Organocatalytic and direct asymmetric vinylogous Michael addition of $\alpha,\alpha$ -dicyanoolefins to $\alpha,\beta$ -unsaturated aldehydes

Jian-Wu Xie, Lei Yue, Dong Xue, Xiao-Li Ma, Ying-Chun Chen,\* Yong Wu, Jin Zhu and Jin-Gen Deng\*

The first highly regio-, chemo-, diastereo- and enantioselective direct vinylogous Michael addition of dicyanoolefins to unsaturated aldehydes is described.



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