## ChemComm

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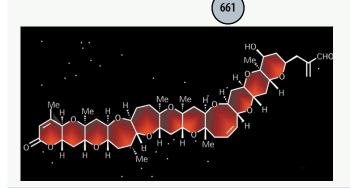


Cover The universe of transition-metal

The universe of transition-metal-containing chiral bidentate ligands is rapidly expanding, and is symbolized on the cover as a solar system with a ferrocene-based sun and celestial bodies featuring ligands and metals that play a prominent role in the feature article.

> Chemical biology articles published in this journal also appear in the Chemical Biology Virtual Journal: www.rsc.org/chembiol

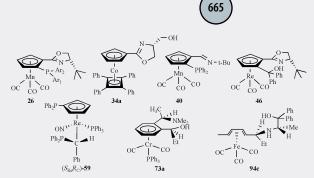
# Contents



#### Creating complexity - the beauty and logic of synthesis

K. C. Nicolaou

The author's work in the total synthesis of natural products, marked by the conquest of some extraordinarily challenging target compounds, is described.



#### CATURE ARTICLE

Transition-metal-containing chiral bidentate ligands for enantioselective catalysis: non-metallocene architectural units come of age

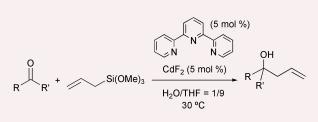
Olivier Delacroix and John A. Gladysz\*

The title paradigm represents an exciting new frontier for ligand design for metal-catalyzed enantioselective reactions, some examples of which include 26, 34a, 40, 46,  $(S_{Re}R_C)$ -59, 73a, and 94c.

#### COMMUNICATIONS

### Allylation reactions of carbonyl compounds using an organosilicon reagent in aqueous media

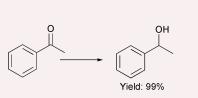
Naohiro Aoyama, Tomoaki Hamada, Kei Manabe and Shu Kobayashi\*



676

Allylation reactions of carbonyl compounds such as aldehydes and reactive ketones using allyltrimethoxysilane in aqueous media proceeded smoothly in the presence of 5 mol% of a  $CdF_2$ -terpyridine complex.

i



Reagents and conditions: 10 mol% Pd<sup>0</sup>-EnCat, 0.8 mmol HCOOH, 0.8 mmol Et<sub>3</sub>N, 200 μL EtOAc, 24 °C, 21 hrs



682

686

678

### Transfer hydrogenation using recyclable polyurea-encapsulated palladium: efficient and chemoselective reduction of aryl ketones

Jin-Quan Yu, Hai-Chen Wu, Chandrashekar Ramarao, Jonathan B. Spencer\* and Steven V. Ley\*

The treatment of polyurea-encapsulated palladium(II) acetate with formic acid provides a robust and recyclable palladium catalyst [Pd<sup>0</sup>EnCat] which is demonstrated to be an efficient and chemoselective transfer hydrogenation catalyst for the reduction of aryl ketones.

#### Covalent crosslinking of 1-D photonic crystals of microporous Si by hydrosilylation and ring-opening metathesis polymerization

Myeong Sik Yoon, Kyo Han Ahn,\* Ronnie W. Cheung, Honglae Sohn, Jamie R. Link, Frédérique Cunin and Michael J. Sailor\*



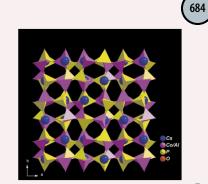
*situ*" ring-opening metathesis polymerization in porous Si multilayer dielectric mirrors, in which poly(norbornene) is covalently attached to the porous Si matrix.

A flexible and stable composite photonic material is prepared by "in

#### A novel synthetic strategy for hexanuclear supramolecular architectures

Oleg V. Dolomanov, Alexander J. Blake, Neil R. Champness,\* Martin Schröder and Claire Wilson

Hexanuclear cage complexes  $[M_6L_6X](X)_5$   $[M = Cu(I), Ag(I); L = 6,6'-bis(4-ethynylpyridine)2,2'-bipyridine; X = BF_4^-, SbF_6^-]$  have been prepared using a self-assembly approach; these architectures encapsulate anions in the solid-state and are fluxional in solution.



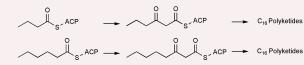
## High temperature synthesis of a noncentrosymmetric site-ordered cobalt aluminophosphate related to the pollucite structure

J. P. Hirst, J. B. Claridge, M. J. Rosseinsky and P. Bishop

Partial Co<sup>2+</sup> and Al<sup>3+</sup> ordering over the tetrahedral sites produces a noncentrosymmetric decoration of the pollucite network accessible by high-temperature synthesis.

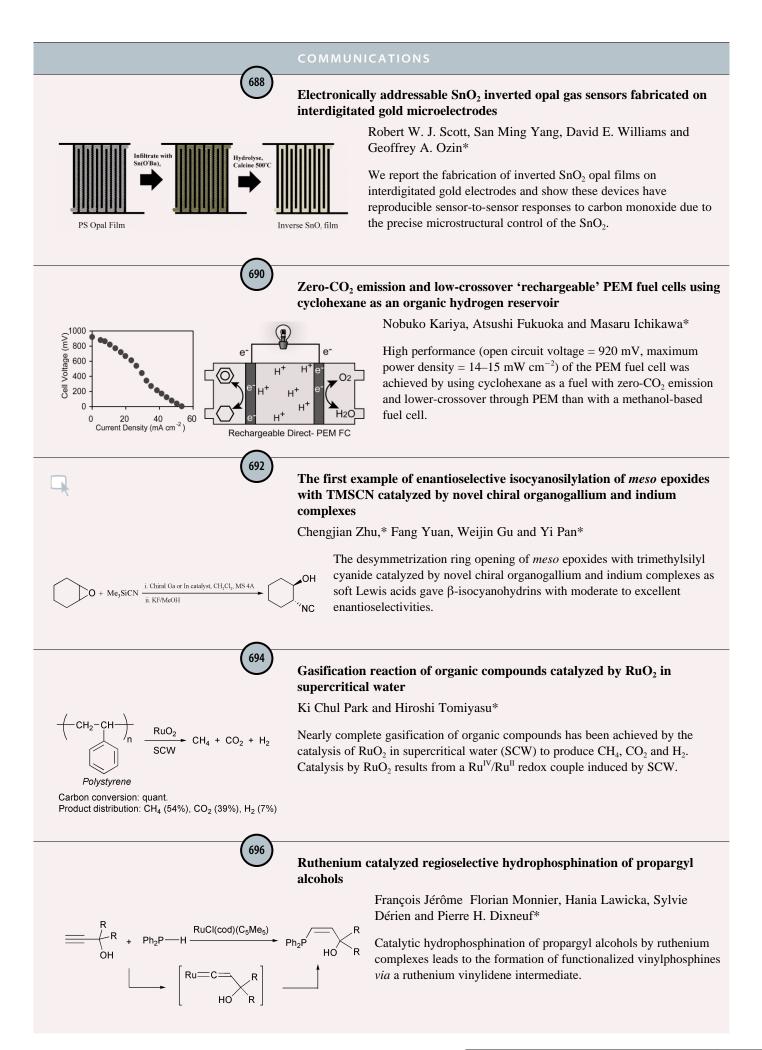
## First *in vitro* directed biosynthesis of new compounds by a minimal type II polyketide synthase: evidence for the mechanism of chain length determination

T. P. Nicholson, C. Winfield, J. Westcott, J. Crosby, T. J. Simpson and R. J. Cox\*

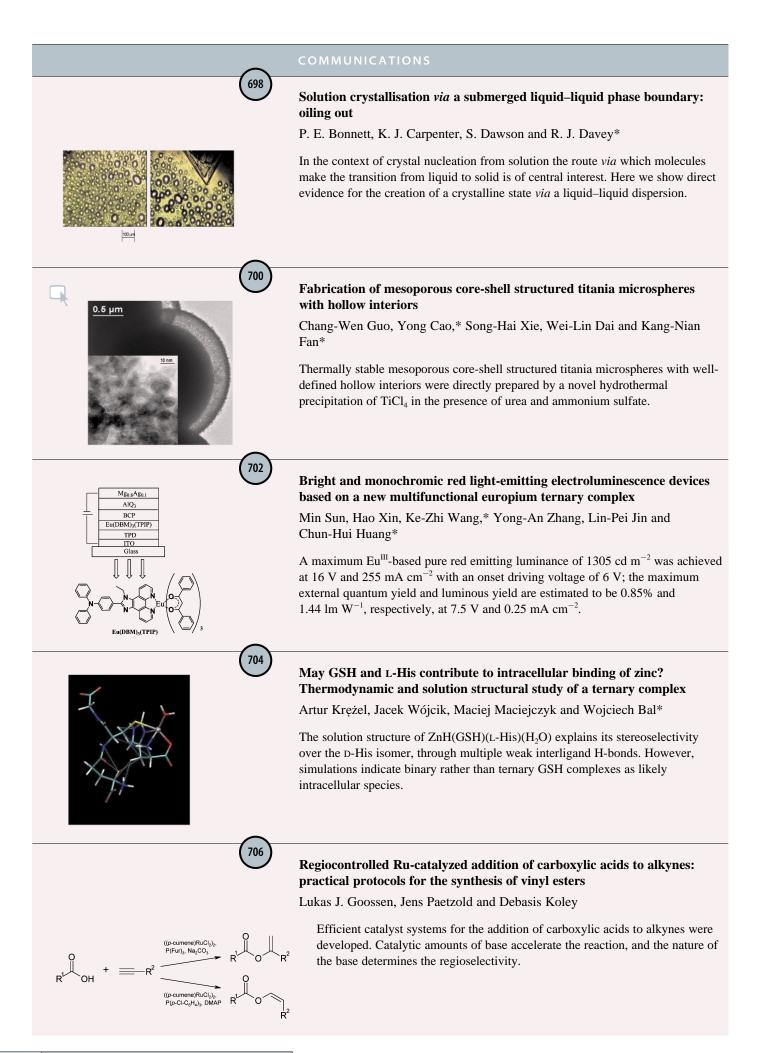


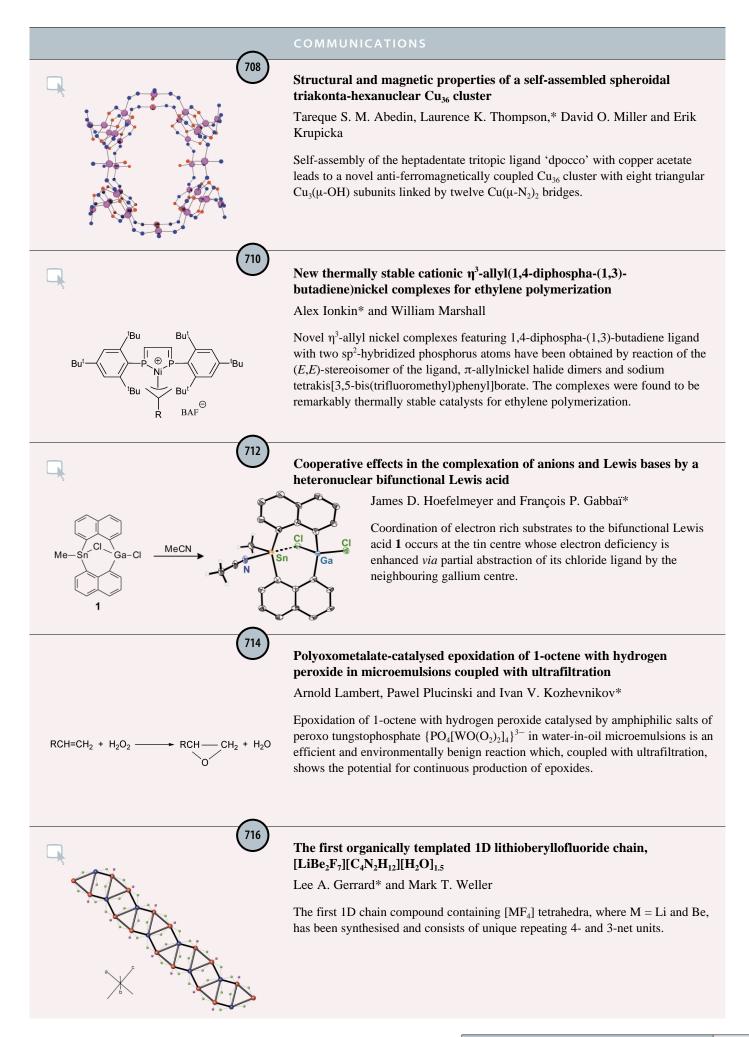
Reactions catalysed by the purified actinorhodin minimal polyketide synthase (PKS) *in vitro* give rise to new  $C_{16}$  polyketides regardless of the length of the starter unit. This gives the first experimental evidence that type II PKS control chain length by measuring.

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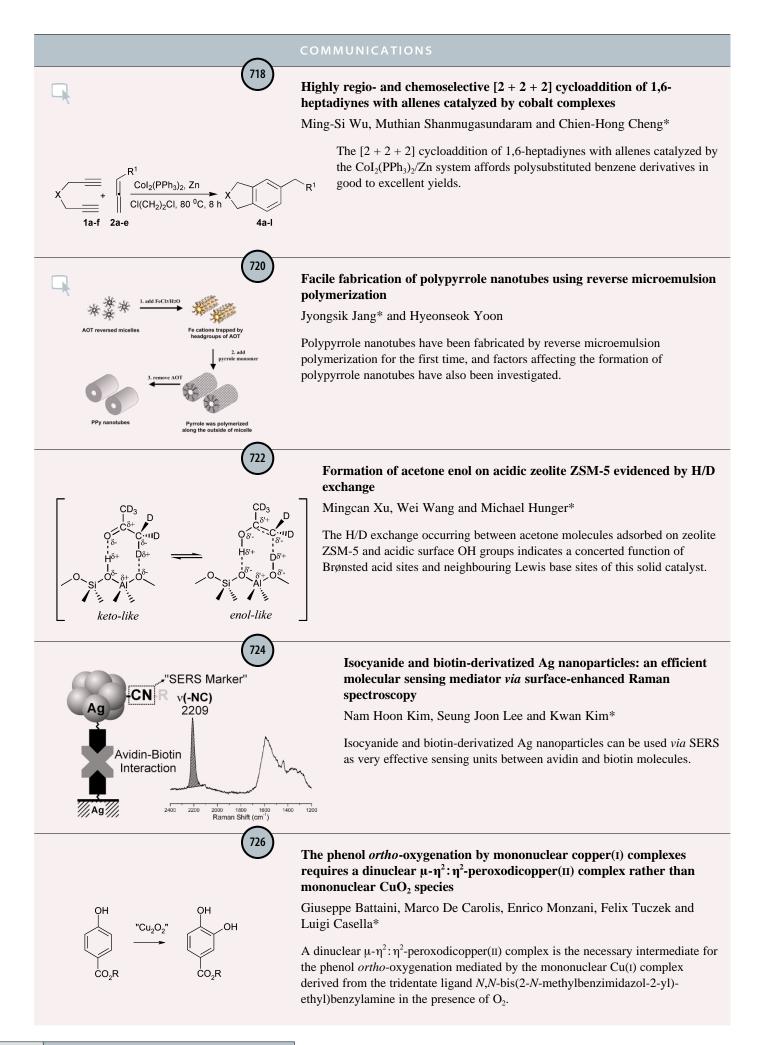


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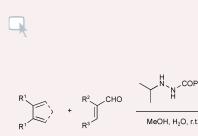




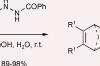
v



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R<sup>2</sup> = H, Me R<sup>3</sup> = H, Me, Ph



732

53 - 89 % e.e

734

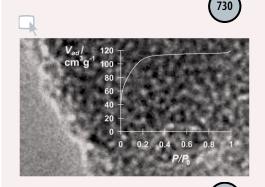
736

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Iminium ion catalysis: Use of the  $\alpha\text{-effect}$  in the acceleration of the Diels–Alder reaction

Julie L. Cavill, Jens-Uwe Peters and Nicholas C. O. Tomkinson\*

The  $\alpha$ -effect can be used as an effective platform for iminium ion catalysis, providing acyclic structures capable of catalysing the Diels–Alder reaction.



MgCl

Ph

ca. 90 % e.e

#### Template assisted design of microporous gallium nitride materials

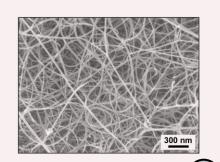
Gérald Chaplais, Klaus Schlichte, Oliver Stark, Roland A. Fischer and Stefan Kaskel\*

Highly porous GaN materials with pore sizes below 2 nm and extremely high internal surface area comparable to zeolitic solids were obtained using an amine assisted molecular precursor condensation reaction.

### Kumada–Corriu coupling of Grignard reagents, probed with a chiral Grignard reagent

Bettina Hölzer and Reinhard W. Hoffmann\*

Kumada–Corriu coupling of a chiral Grignard reagent proceeded with full retention of configuration or with partial racemisation depending on the catalyst used.



MX<sub>n</sub>L<sub>n</sub>

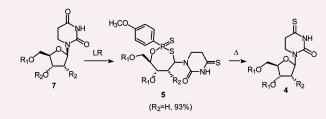
-78°C,

## Synthesis of high-quality single-walled carbon nanotubes by catalytic decomposition of $C_2 H_2$

S. C. Lyu, B. C. Liu, T. J. Lee, Z. Y. Liu, C. W. Yang, C. Y. Park and C. J. Lee\*

High-quality single-walled carbon nanotubes free of defects and amorphous carbon coating have been produced by catalytic decomposition of  $C_2H_2$  over Fe–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.

## Thiation of 2'-deoxy-5,6-dihydropyrimidine nucleosides with Lawesson's reagent: Characterisation of oxathiaphosphepane intermediates



Frédéric Peyrane, Jean-Louis Fourrey and Pascale Clivio\*

Oxathiaphosphepane nucleosides are formed upon the treatment of dihydropyrimidine nucleosides with Lawesson's reagent. The incorporation of the  $AnPS_2$  unit within the furane ring is heat reversible and allows the attainment of the C4-thiolated compounds.

738

740

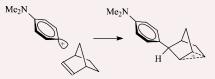
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746

#### A novel access to 3-aryl-2-norbornyl cation

Mariella Mella, Silvia Esposti, Maurizio Fagnoni and Angelo Albini



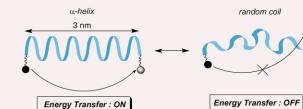
Addition to norbornene of 4-aminophenyl cation formed by photoheterolysis of chloroaniline in MeCN or alcohols offers a novel entry to a 2-norbornyl cation under mild, non acidic conditions.

#### Construction of extended networks with a trimeric pyrazole synthon

Ishtvan Boldog, Eduard B. Rusanov, Joachim Sieler, Steffen Blaurock and Konstantin V. Domasevitch\*

Self-association of bifunctional bipyrazole generates highly interpenetrated 3D frameworks. The study features effective control over degree of the interpenetration and a rational approach for crystallization of a novel polymorph.

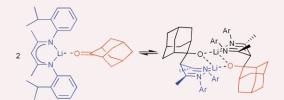
#### A distance-controlled oligopeptide linker as a novel photo-induced energy transfer switch by secondary structural transition



Akira Kishimoto, Toshiki Mutai and Koji Araki\*

By using an oligopeptide chain as a functional linker and introducing coumarin 2 and coumarin 343 at the chain ends, a distance-controlled photo-induced energy transfer switch induced by a helix–coil transition of the linker was constructed.

Reversible C–C bond formation: solid state structure of the aldol-like addition product of adamantanone to a 1,5-diazapentadienyllithium, and its solution state retro-aldol dissociation

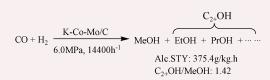


Lee-Jon Ball, Anthony P. Dickie, Francis S. Mair,\* David A. Middleton and Robin G. Pritchard

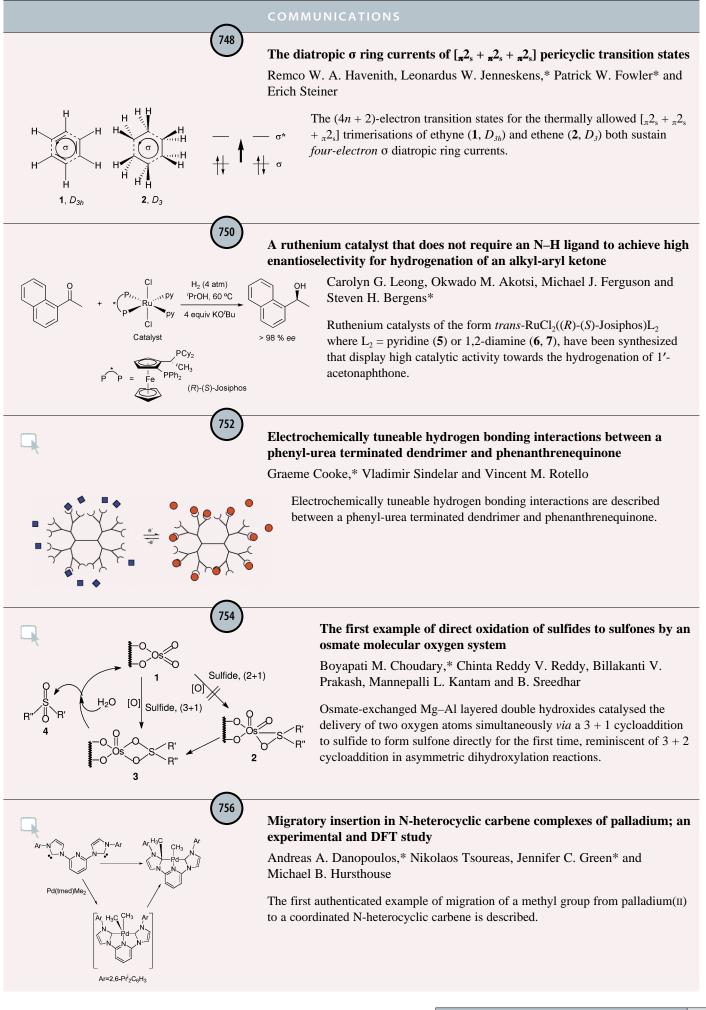
Crystals of the lithium diimine alkoxide formed upon addition of adamantanone to a 1,5-diazapentadienyllithium complex display a long C–C bond which ruptures upon dissolution in non-co-ordinating solvents.

## A highly active K-Co-Mo/C catalyst for mixed alcohol synthesis from CO + $\rm H_2$

Jun Bao,\* YiLu Fu, ZhongHai Sun and Chen Gao



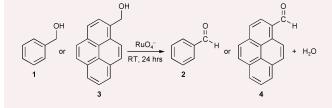
A highly homogeneous, highly dispersed K-Co-Mo/C catalyst has been prepared for the first time by a simple sol–gel method. It exhibits much higher alcohol yield, especially higher  $C_{2+}OH$  selectivity for mixed alcohol synthesis from CO + H<sub>2</sub> than those of similar catalyst systems reported.



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#### Shape-selective oxidation of primary alcohols using perruthenatecontaining zeolites

Daniel L. Wu, Andrea P. Wight and Mark E. Davis\*



760

762

764

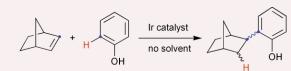
766

Potassium perruthenate ( $KRuO_4$ ) is impregnated into zeolite X and shown to be a shape-selective oxidant using benzyl alcohol (reacted) and pyrenemethanol (not reacted).

## Addition of the *ortho*-C–H bonds of phenol across an olefin catalysed by a chiral iridium(I) diphosphine complex

Romano Dorta\* and Antonio Togni

Kamal Amani



A chiral iridium(I) complex catalyses the atom-economical, solvent-free *ortho*-alkylation of phenol with norbornene *via* C–H activation to form new C–C bonds.

## Structure and magnetism of the first strictly dinuclear compound containing paramagnetic 3d and 5f metal ions. Major influence of the Cu<sup>II</sup> ion coordination on the exchange Cu<sup>II</sup>–U<sup>IV</sup> interaction

Lionel Salmon,\* Pierre Thuéry, Eric Rivière, Jean-Jacques Girerd and Michel Ephritikhine\*

In the complex represented here, the Cu–U interaction is antiferromagnetic; comparison of the magnetic properties of trinuclear  $Cu_2U$  compounds with different Schiff base ligands indicates that the Cu(II) ion coordination has a strong influence on the Cu–U exchange interaction.

## Aluminium dodecatungstophosphate (AlPW<sub>12</sub>O<sub>40</sub>) as a highly efficient catalyst for the selective acetylation of -OH, -SH and $-NH_2$ functional groups in the absence of solvent at room temperature

Habib Firouzabadi,\* Nasser Iranpoor,\* Farhad Nowrouzi and

Catalytic amount of aluminium dodecatungstophosphate (AlPW<sub>12</sub>O<sub>40</sub>,

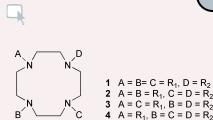
0.001 mmol) as a water stable and a non-hygroscopic compound has

been used effectively for the selective acetylation of -OH, NH<sub>2</sub>, and

R-XH  $\xrightarrow{\text{Ac}_2\text{O} (1.5 \text{ mmol}), \text{AlPW}_{12}\text{O}_{40}(0.001 \text{ mmol})}$  R-XAc

X = O, NH, S

R = alkyl(1°, 2°, 3°),benzyl aryl, allyl,propargyl



 $R_1 = CH_2CO_2H$  $R_2 = CH_2Ph(4-tBu)$ 

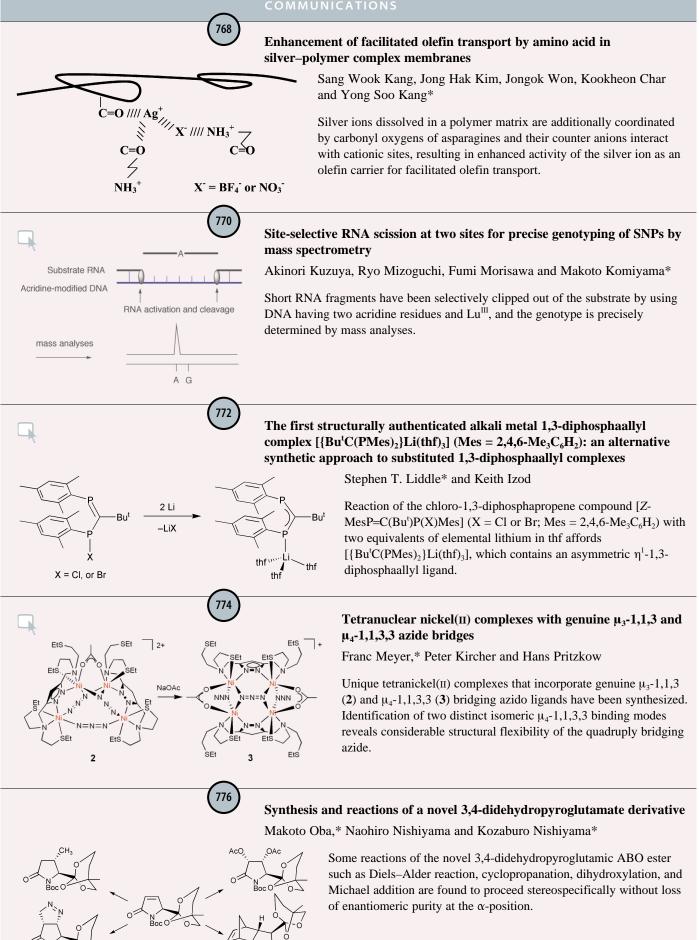
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## **Regioselective** *N***-substitution of cyclen with two different alkyl groups:** synthesis of all possible isomers

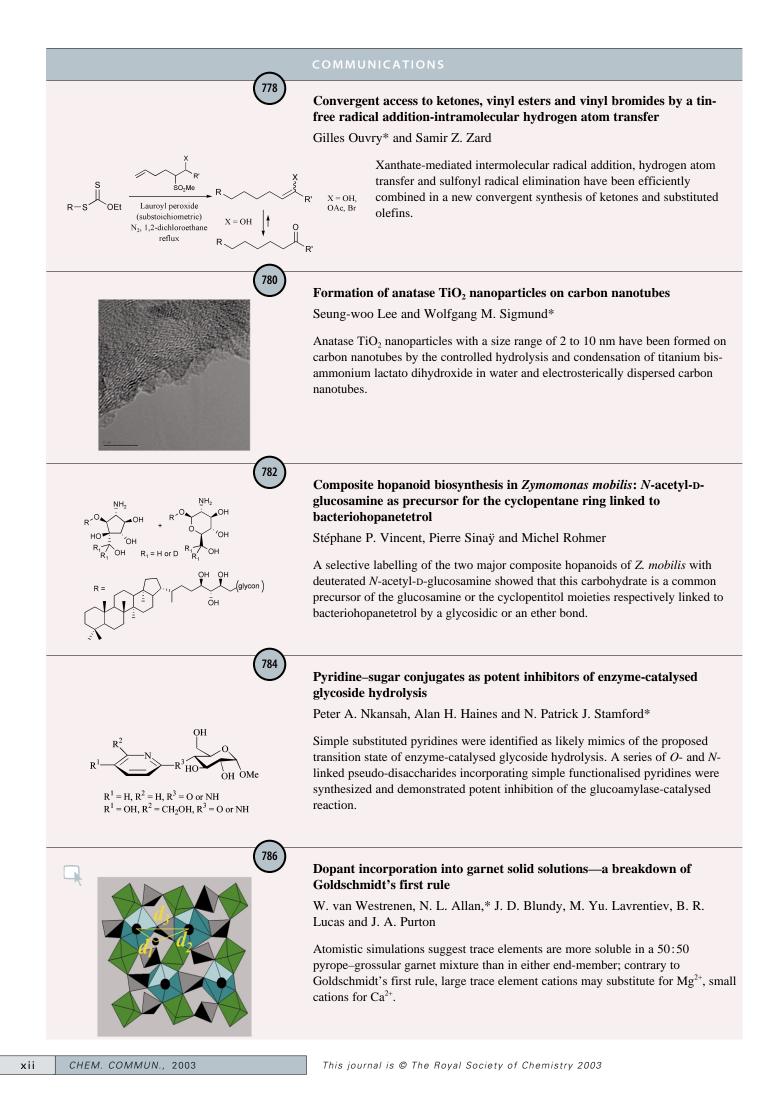
-SH in the absence of solvent at room temperature.

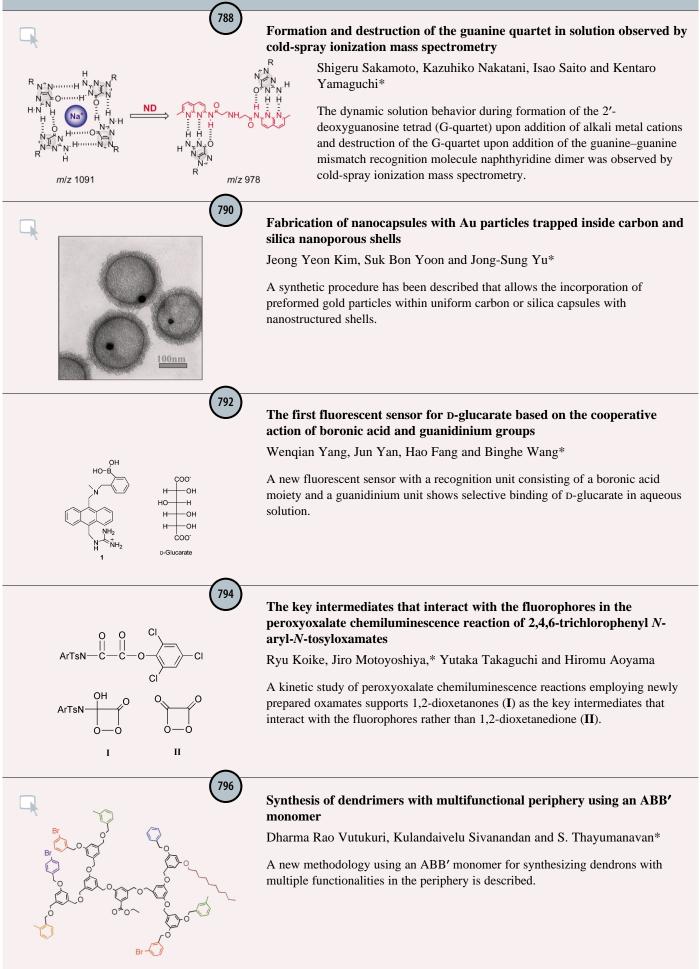
Jeongsoo Yoo, David E. Reichert and Michael J. Welch\*

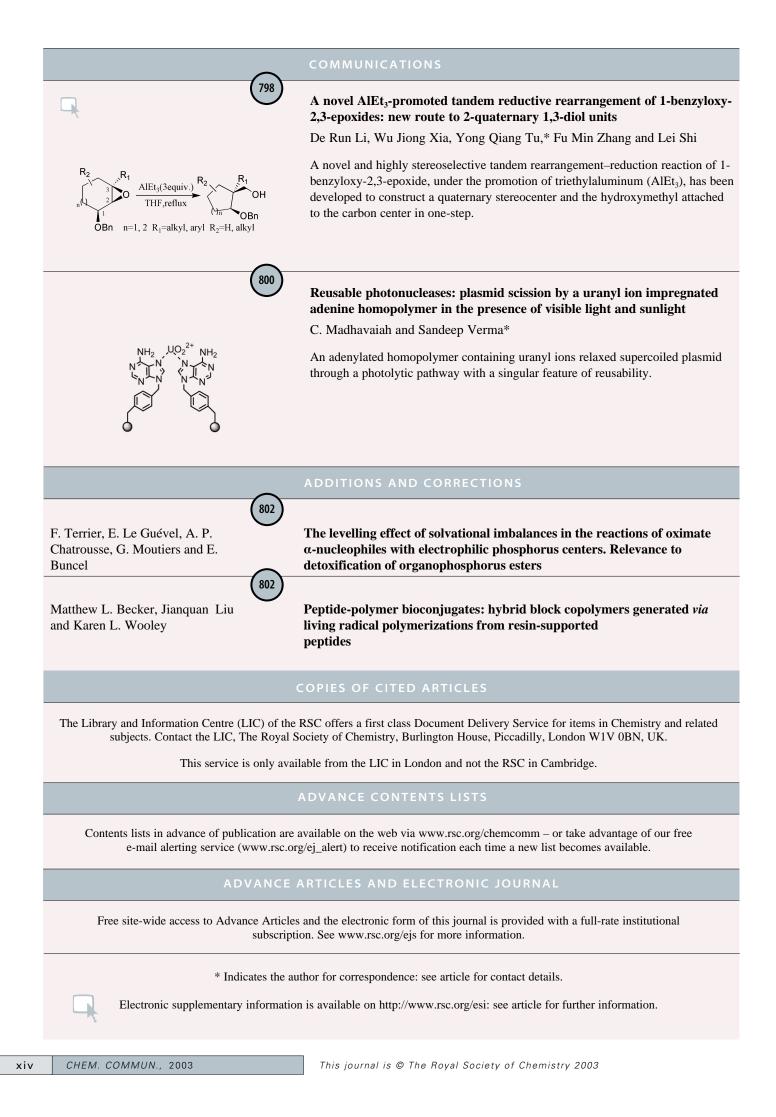
All possible configurations of two different groups on the four nitrogen atoms of cyclen were achieved using four differently protected cyclen intermediates including the novel mono-protected cyclen compound, mono-*N*-Cbz-cyclen.



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NOTE: An asterisk in the heading of each paper indicates the author who is to receive any correspondence.