

# Green Chemistry

Cutting-edge research for a greener sustainable future

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## IN THIS ISSUE

ISSN 1463-9262 CODEN GRCHFJ 12(9) 1481–1676 (2010)



### Cover

See Luque and Varma *et al.*, pp. 1540–1543. Magnetically separable and anchored glutathione catalyzes the homocoupling of boronic acids in water under the influence of microwave irradiation.

Image reproduced by permission of Rafael Luque from *Green Chemistry*, 2010, **12**, 1540.

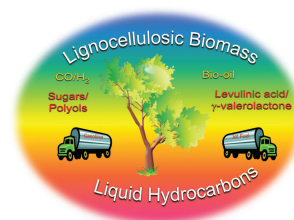
## CRITICAL REVIEWS

1493

### Catalytic conversion of biomass to biofuels

David Martin Alonso, Jesse Q. Bond and James A. Dumesic\*

Catalytic conversion of lignocellulosic biomass to liquid hydrocarbon fuels through intermediate formation of synthesis gas, bio-oil, sugars, polyols, levulinic acid, and/or  $\gamma$ -valerolactone.

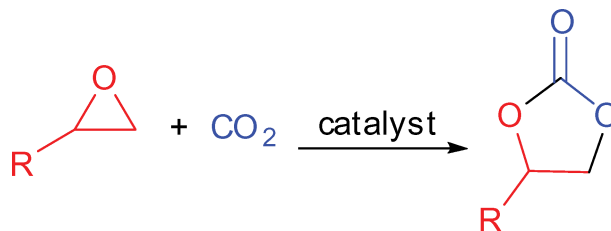


1514

### Synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>

Michael North,\* Riccardo Pasquale and Carl Young

The synthesis of cyclic carbonates from epoxides and CO<sub>2</sub> is reviewed with emphasis on the green credentials of the reaction.



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# Green Chemistry

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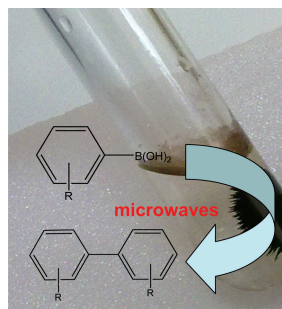
## COMMUNICATIONS

1540

**Magnetically separable nanoferrite-anchored glutathione: aqueous homocoupling of arylboronic acids under microwave irradiation**

Rafael Luque,\* Babita Baruwati and Rajender S. Varma\*

A nanoferrite-glutathione catalyst was found to promote the homocoupling of boronic acids in water under microwave irradiation

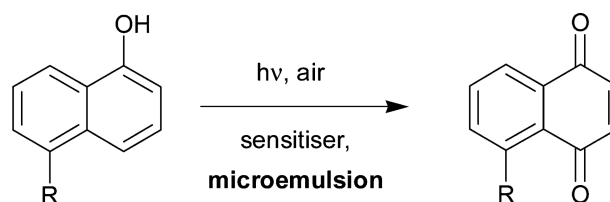


1544

**Green photochemistry: the use of microemulsions as green media in photooxygenation reactions**

Emma E. Coyle, Kieran Joyce, Kieran Nolan and Michael Oelgemöller\*

The use of microemulsions as green media for photooxygenation reactions was investigated.

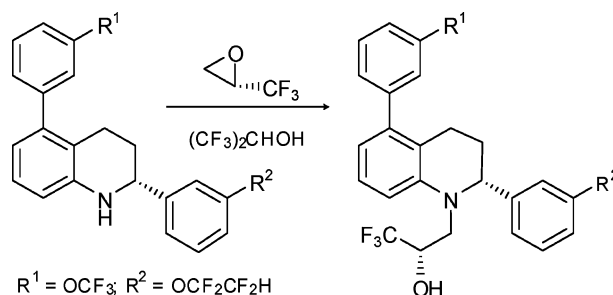


1548

**Regio- and diastereoselective ring-opening of (*S*)-(-)-2-(trifluoromethyl)oxirane with chiral 2,5-disubstituted tetrahydroquinolines in hexafluoro-2-propanol**

Xun Li,\* Ronald K. Russell, Hongfeng Chen, Yongzheng Zhang, Scott Ballentine, Jan Spink, Shawn Branum, Fuqiang Liu, Yanping Chen, Thomas Rammeloo, Wim Aelterman, Kirk L. Sorgi and William V. Murray

Treatment of optically pure (*S*)-(-)-2-(trifluoromethyl)oxirane and chiral 2,5-disubstituted tetrahydroquinoline in hexafluoro-2-propanol afforded a quantitative and diastereomerically pure product.

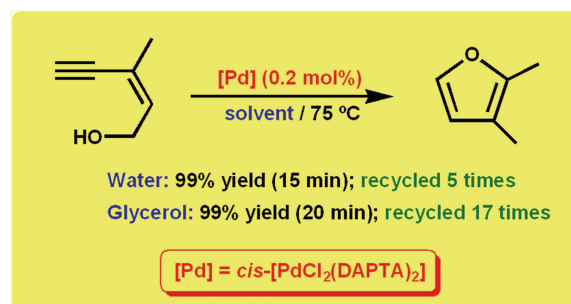


1552

**Palladium-catalyzed cycloisomerization of (*Z*)-enynols into furans using green solvents: glycerol vs. water**

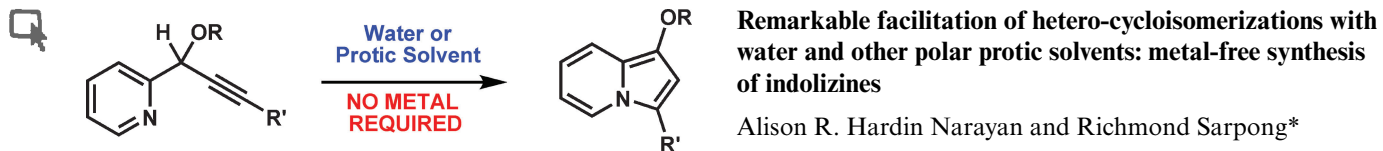
Javier Francos and Victorio Cadierno\*

Palladium-catalyzed heteroannulation reactions of (*Z*)-en-4-yn-1-ol derivatives into furans have been studied using water and glycerol as alternative green reaction media. Higher activities were observed in water, but catalyst recycling was much more effective in glycerol.



## COMMUNICATIONS

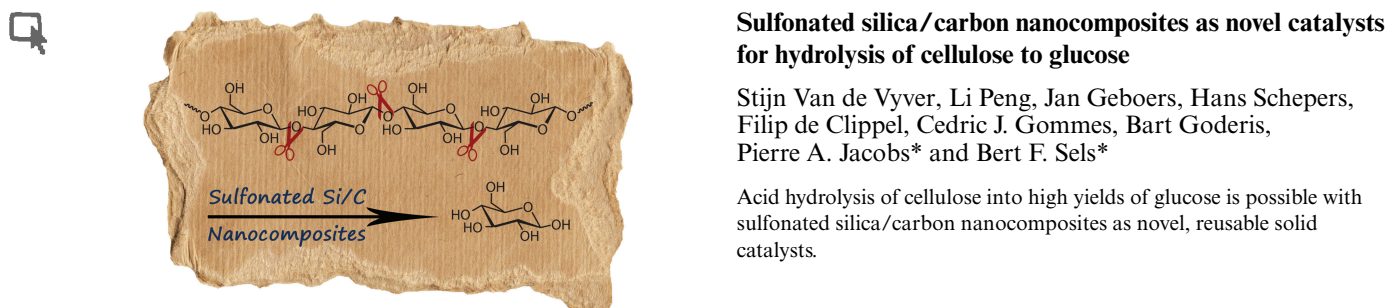
1556



Alison R. Hardin Narayan and Richmond Sarpong\*

A synthesis of indolizines, which had been previously reported to proceed with metal catalysts, has been shown to proceed with water alone or in polar protic solvents.

1560



Stijn Van de Vyver, Li Peng, Jan Geboers, Hans Schepers, Filip de Clippel, Cedric J. Gommaes, Bart Goderis, Pierre A. Jacobs\* and Bert F. Sels\*

Acid hydrolysis of cellulose into high yields of glucose is possible with sulfonated silica/carbon nanocomposites as novel, reusable solid catalysts.

1564

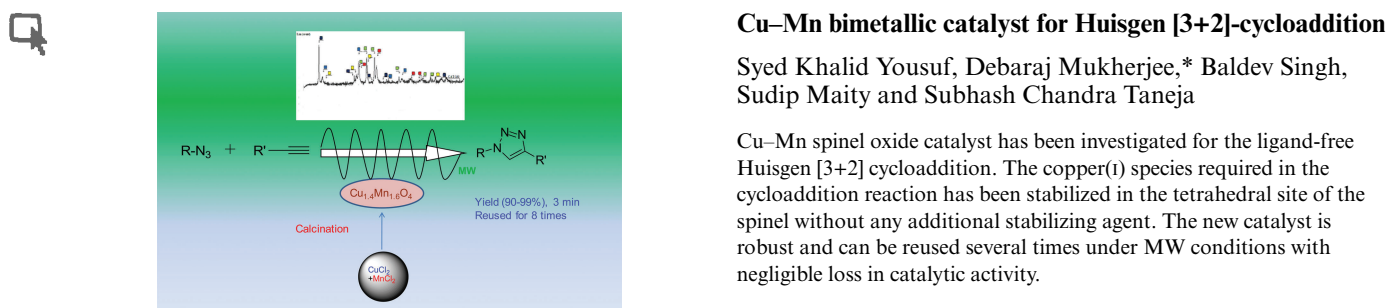


Microbially-synthesized glycolipids can be used as new, entirely sustainable, structure-directing agents in the synthesis of inorganic porous oxides

Niki Baccile,\* Nadine Nassif, Luca Malfatti, Inge N. A. Van Bogaert, Wim Soetaert, Gerard Pehau-Arnaudet and Florence Babonneau

Microbially-synthesized glycolipids can be used as new, entirely sustainable, structure-directing agents in the synthesis of inorganic porous oxides.

1568



Syed Khalid Yousuf, Debaraj Mukherjee,\* Baldev Singh, Sudip Maity and Subhash Chandra Taneja

Cu–Mn spinel oxide catalyst has been investigated for the ligand-free Huisgen [3+2] cycloaddition. The copper(I) species required in the cycloaddition reaction has been stabilized in the tetrahedral site of the spinel without any additional stabilizing agent. The new catalyst is robust and can be reused several times under MW conditions with negligible loss in catalytic activity.



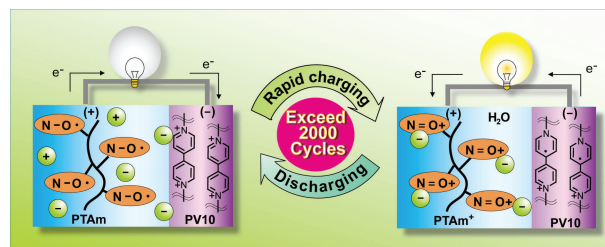
## COMMUNICATIONS

1573

**A TEMPO-substituted polyacrylamide as a new cathode material: an organic rechargeable device composed of polymer electrodes and aqueous electrolyte**

Kenichiroh Koshika, Natsuru Chikushi, Naoki Sano, Kenichi Oyaizu and Hiroyuki Nishide\*

Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide) was designed and synthesized as an electrode-active polymer for an aqueous electrolyte-type organic rechargeable device which demonstrated a 1.2 V output voltage and exceeded 2000 charging–discharging cycles.

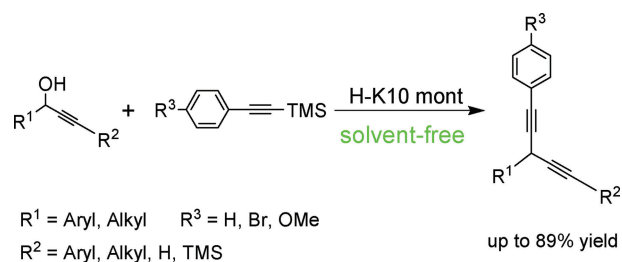


1576

**Solvent-free solid acid-catalyzed nucleophilic substitution of propargylic alcohols: a green approach for the synthesis of 1,4-diyne**

Tao Wang, Rui-da Ma, Liu Liu and Zhuang-ping Zhan\*

A solvent-free solid acid-catalyzed nucleophilic substitution of propargylic alcohols with alkynylsilanes is described.



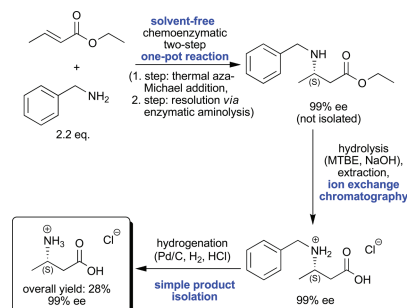
## PAPERS

1580

**Towards a greener synthesis of (*S*)-3-aminobutanoic acid: process development and environmental assessment**

Markus Weiß, Tobias Brinkmann and Harald Gröger\*

An improved, greener chemoenzymatic process was developed for the enantioselective multi-step synthesis of (*S*)-3-amino butanoic acid, which was obtained with 99% ee. In addition, a detailed environmental assessment of the overall process was done.

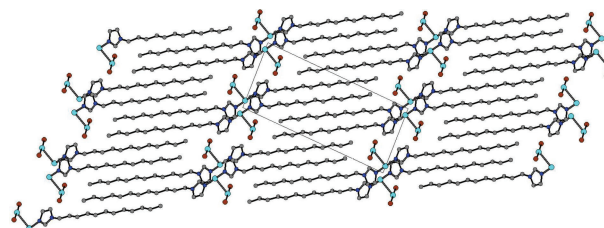


1589

**Cu(I)/(II) based catalytic ionic liquids, their metallo-laminate solid state structures and catalytic activities in oxidative methanol carbonylation**

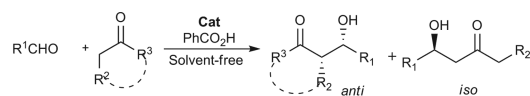
Marion Stricker, Thomas Linder, Benjamin Oelkers and Jörg Sundermeyer\*

Novel cupronium cuprate ionic liquids reveal not only interesting laminate structures, but also catalytic activity in the oxidative carbonylation of methanol to dimethyl carbonate.

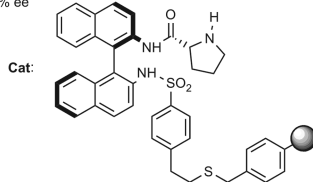


## PAPERS

1599



$R^2, R^3 = \text{Cycloalkyl}; R^2 = \text{H, CH}_3, \text{OMe, SMe}, R^3 = \text{CH}_3 \text{ or } R^2 = \text{CH}_3, R^3 = \text{H}$   
*anti/iso* up to 17:83, *anti/syn* up to 95:5; 73–88 % ee

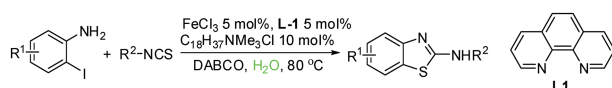


### Solvent-free direct enantioselective aldol reaction using polystyrene-supported *N*-sulfonyl-( $R_4$ )-binam-D-prolinamide as a catalyst

Abraham Bañón-Caballero, Gabriela Guillena\* and Carmen Nájera\*

Polystyrene-supported *N*-sulfonyl-( $R_4$ )-binam-D-prolinamide was used as an efficient catalyst for the enantioselective direct aldol reaction under solvent-free or aqueous conditions, with catalyst recovery and reuse being possible.

1607

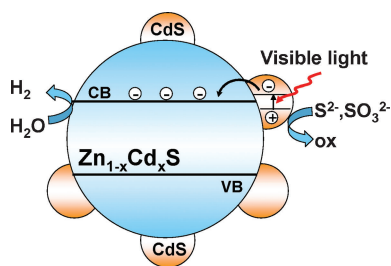


### Synthesis of 2-aminobenzothiazole *via* FeCl<sub>3</sub>-catalyzed tandem reaction of 2-iodoaniline with isothiocyanate in water

Qiuping Ding,\* Banpeng Cao, Xianjin Liu, Zhenzhen Zong and Yi-Yuan Peng\*

An FeCl<sub>3</sub>-catalyzed tandem reaction of 2-iodoaniline with isothiocyanate in pure water is described, which provides an environmentally benign, efficient, and practical route for the synthesis of 2-aminobenzothiazole. The reaction media can be recovered and recycled.

1611

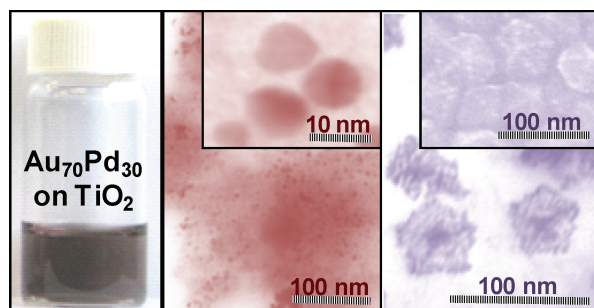


### Preparation and enhanced visible-light photocatalytic H<sub>2</sub>-production activity of CdS quantum dots-sensitized Zn<sub>1-x</sub>Cd<sub>x</sub>S solid solution

Jiaguo Yu,\* Jun Zhang and Mietek Jaroniec\*

CdS quantum dot-sensitized Zn<sub>1-x</sub>Cd<sub>x</sub>S materials show high visible-light photocatalytic H<sub>2</sub>-production activity in aqueous solutions containing Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S sacrificial reagents.

1615



### Environmentally benign aqueous oxidative catalysis using AuPd/TiO<sub>2</sub> colloidal nanoparticle system stabilized in absence of organic ligands

Andrew J. Frank, Jacob Rawski, Kenneth E. Maly\* and Vladimir Kitaev\*

A novel preparation of an entirely inorganically stabilized colloidal gold-palladium nanoparticle system supported on dispersed aqueous titania is described; applications of this system in green oxidative catalysis that can use atmospheric oxygen are demonstrated.

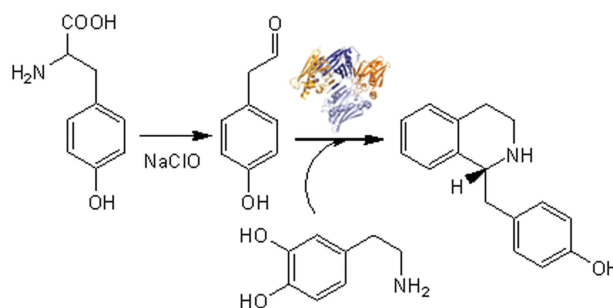
## PAPERS

1623

**An enzymatic, stereoselective synthesis of (*S*)-norcoclaurine**

Alessandra Bonamore, Irene Rovardi, Francesco Gasparrini, Paola Baiocco, Marco Barba, Carmela Molinaro, Bruno Botta, Alberto Boffi and Alberto Macone\*

An efficient, stereoselective, green synthesis of (*S*)-norcoclaurine (higenamine) has been developed using the recombinant (*S*)-norcoclaurine synthase (NCS) enzyme, in a one-pot, two step process.

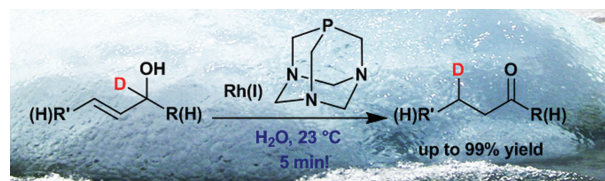


1628

**Rhodium-catalysed isomerisation of allylic alcohols in water at ambient temperature**

Nanna Ahlsten, Helena Lundberg and Belén Martín-Matute\*

Primary and secondary allylic alcohols are isomerised at ambient temperature in water using a commercially available cationic rhodium complex. Yields of up to 99% can be achieved in only five minutes. Mechanistic investigations and deuterium labelling studies are presented.

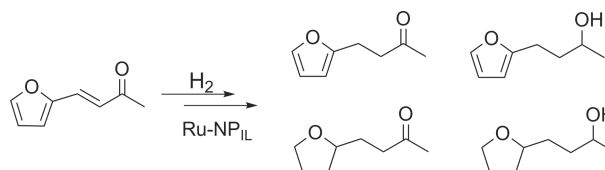


1634

**Selective hydrogenation of biomass derived substrates using ionic liquid-stabilized ruthenium nanoparticles**

Jennifer Julis, Markus Hölscher and Walter Leitner\*

Careful control of the catalytic system and the reaction conditions allows the selective synthesis of a variety of substituted furans from biomass derived 4-(2-furyl)-3-butene-2-one by using IL-stabilized ruthenium nanoparticles.

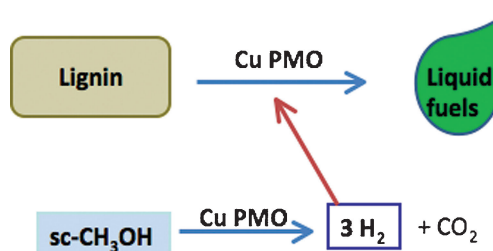


1640

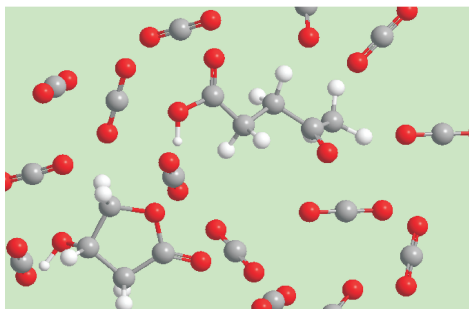
**Catalytic disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol**

Katalin Barta, Theodore D. Matson, Makayla L. Fettig, Susannah L. Scott, Alexei V. Iretskii\* and Peter C. Ford\*

Described is the novel one-pot catalytic disassembly of biomass-derived organosolv lignin in supercritical methanol.



1648



### Solubility of bio-sourced feedstocks in 'green' solvents

Samantha M. Payne and Francesca M. Kerton\*

Renewable dicarboxylic acids are soluble in methanol-modified carbon dioxide, whereas levulinic acid and 3-hydroxybutyrolactone are soluble in neat carbon dioxide.

1654

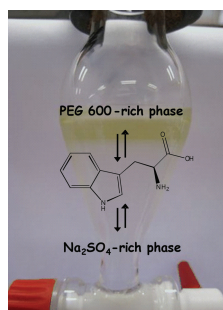


### Phosphonium nitrate ionic liquid catalyzed electrophilic aromatic oxchlorination

Marco Noè, Alvis Perosa,\* Maurizio Selva and Luca Zambelli

The catalytic electrophilic aromatic chlorination of arenes with HCl and nitrate ionic liquids is investigated, with emphasis on the optimization of the conditions, and on catalyst recycling. A mechanism of catalyst regeneration by air is presented.

1661

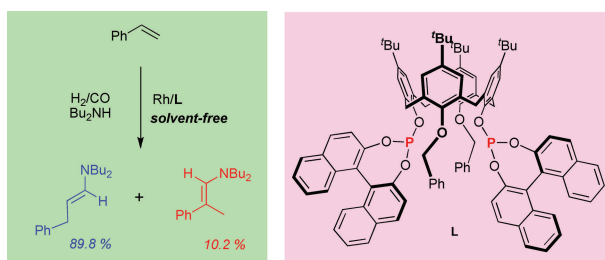


### Ionic liquids as adjuvants for the tailored extraction of biomolecules in aqueous biphasic systems

Jorge F. B. Pereira, Álvaro S. Lima, Mara G. Freire\* and João A. P. Coutinho

The addition of tailored ionic liquids to PEG/inorganic salt aqueous two-phase systems enhances the extraction efficiency for L-tryptophan. This enhancement essentially depends on the nature of the ionic liquid employed.

1670



### Calix[4]arene-diphosphite rhodium complexes in solvent-free hydroaminovinylation of olefins

Laure Monnereau, David Sémeril\* and Dominique Matt\*

Selective, one-pot hydroaminovinylation was achieved under solvent-free conditions with rhodium complexes based on hemispherical diphosphite ligands.

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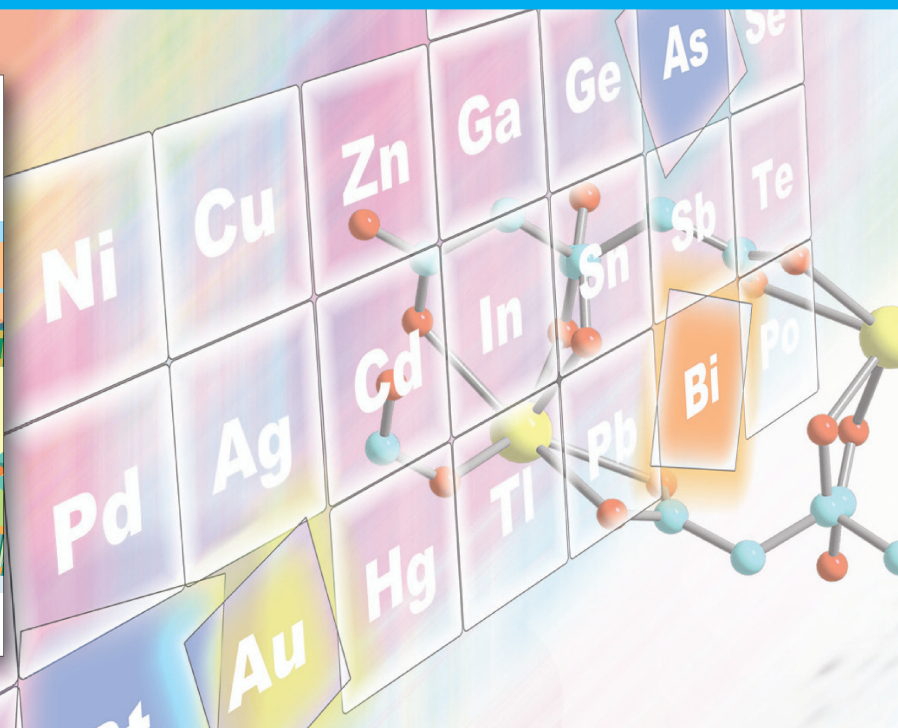


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