**Cover**

See Takeharu Haino *et al.*, page 2321. New self-assembling capsule *via* metal-coordination with a well-defined inner cavity of volume about 580 Å. This discrete guest-binding environment provides unusual complexation of guest molecules as individuals and as pairs. Image reproduced by permission of Takeharu Haino, Mutsumi Kobayashi, Midori Chikaraishi and Yoshimasa Fukazawa from *Chem. Commun.*, 2005, 2321.

**Inside cover**

See Alois Fürstner and Paul W. Davies, page 2307. Two bioactive marine natural products which were successfully prepared by alkyne metathesis as one of the key steps, together with the producing organisms. Image reproduced by permission of Alois Fürstner and Paul W. Davies from *Chem. Commun.*, 2005, 2307.

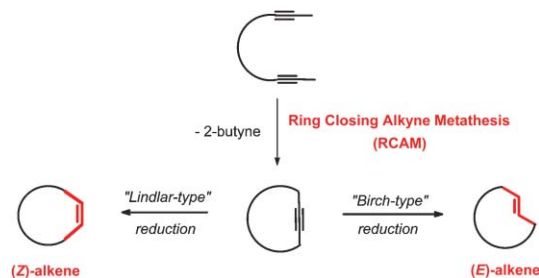
## FEATURE ARTICLE

2307

**Alkyne metathesis**

Alois Fürstner\* and Paul W. Davies

This feature article reviews the present state of the art in the field of alkyne metathesis which has emerged as a valuable synthetic tool applicable in the synthesis of complex molecules and polymer science.



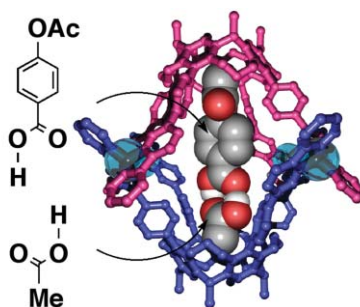
## COMMUNICATIONS

2321

**A new self-assembling capsule *via* metal coordination**

Takeharu Haino,\* Mutsumi Kobayashi, Midori Chikaraishi and Yoshimasa Fukazawa\*

A new cavitant possessing four bipyridine groups was prepared, and forms a stable dimeric molecular capsule *via* metal-coordination in chloroform. The dimeric capsule creates the large cavity in which large aromatic guests accommodate to form the supramolecular complexes. Only the hydrogen-bonded hetero dimer formation in the mixtures of acetic and 4-acetoxybenzoic acids was allowed within the capsule.



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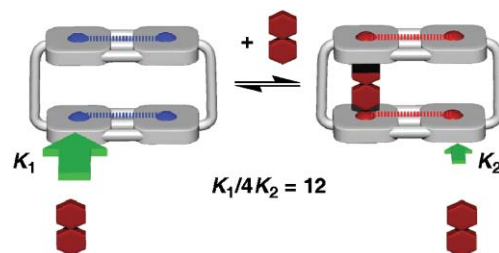
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2324

**Cyclic dimer of a fused porphyrin zinc complex as a novel host with two  $\pi$ -electronically coupled binding sites**

Hiroshi Sato, Kentaro Tashiro, Hideyuki Shinmori, Atsuhiko Osuka and Takuzo Aida\*

Upon complexation with 4,4'-bipyridine, a cyclic dimer of a fused porphyrin zinc complex, having two  $\pi$ -electronically coupled binding sites, shows a strong negative cooperativity in the second guest binding, to allow stepwise formation of 1 : 1 and 1 : 2 inclusion complexes.

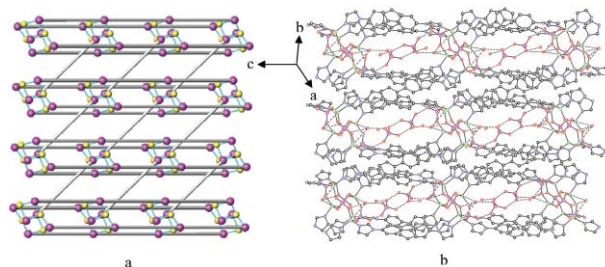


2327

**A two-dimensional cationic lattice built from  $[\text{Zn}_6(\text{HPO}_4)_2(\text{PO}_4)_2]^{2+}$  clusters**

Jian Fan and Brian E. Hanson\*

A unique cationic zinc phosphate cluster linked by neutral bifunctional rigid ligands to form a two dimensional framework was synthesized and structurally characterized.

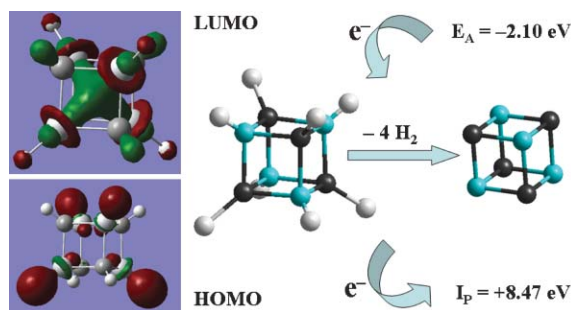


2330

**Theoretical quest for the titanium-substituted hydrocarbons**

Wojciech Grochala\*

We predict, using DFT calculations, that hydrocarbons with half of the carbon atoms substituted by Ti (such as  $\text{Ti}_4\text{C}_4\text{H}_8$  'cubane' shown in the picture), will exhibit sufficient thermodynamic and kinetic stability under ambient conditions. They might be used for moderate-temperature deposition of TiC coatings, and for  $\text{H}_2$  storage.

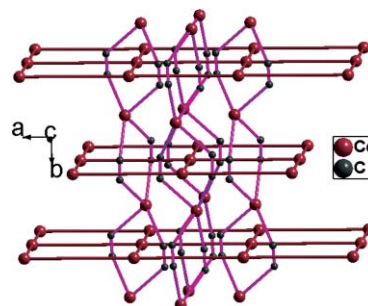


2333

**Supramolecular isomers in the same crystal: a new type of entanglement involving ribbons of rings and 2D (4,4) networks polycatenated in a 3D architecture**

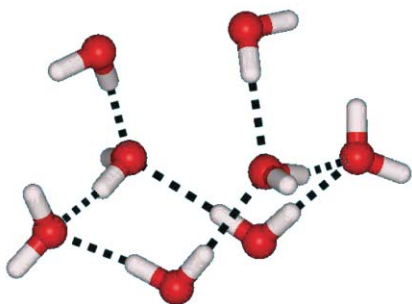
Baolong Li,\* Yanfen Peng, Baozong Li and Yong Zhang

The 3D coordination network  $[\text{Cd}_3(\text{bbtz})_6(\text{H}_2\text{O})_6](\text{BF}_4)_6 \cdot 1.75\text{H}_2\text{O}$  (**1**), containing ribbons of rings and planar 2D (4,4) networks, the undulating 2D (4,4) network  $[\text{Cd}(\text{bbtz})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (**2**), and polymeric ribbons of rings  $[\text{Cd}(\text{bbtz})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot 3\text{DMF}$  (**3**) and  $[\text{Cd}(\text{bbtz})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{DMF}$  (**4**) are obtained.





2336

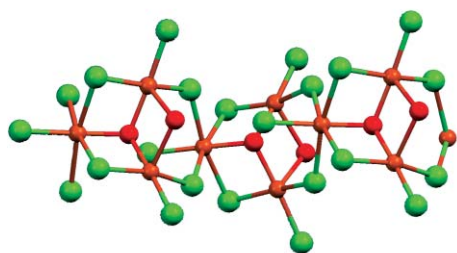


### Observation of an octameric water cluster containing a book-shaped hexamer in a 4f–3d complex

Bao-Qing Ma,\* Hao-Ling Sun and Song Gao\*

A novel well resolved octameric water cluster consisting of a book-shaped cyclic hexamer and two dangling water molecules has been characterized.

2339

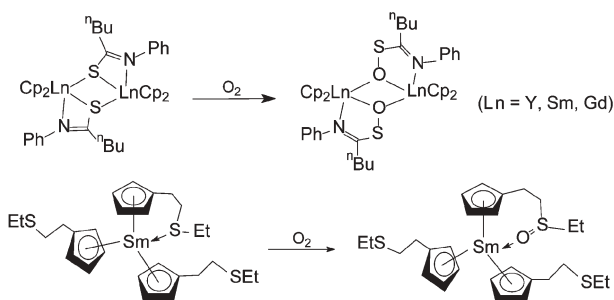


### Structure and magnetic properties of a novel copper halide framework $\{[{}^t\text{BuNH}_3]_2[\text{Cu}_3(\mu_3\text{-OH})(\mu_2\text{-H}_2\text{O})\text{Cl}_7]\}_n$ synthesized *via in situ* templation

Tristram Chivers,\* Zhiyong Fu and Laurence K. Thompson

The use of the tris(alkylamido)phosphate  $\text{OP}[\text{N}(\text{H}){}^t\text{Bu}]_3$  as an *in situ* source of the templating agent  $[{}^t\text{BuNH}_3]^+$  produces the copper halide chain  $\{[{}^t\text{BuNH}_3]_2[\text{Cu}_3(\mu_3\text{-OH})(\mu_2\text{-H}_2\text{O})\text{Cl}_7]\}_n$  in a solvothermal process; the novel antiferromagnetically coupled trinuclear fragment  $\text{Cu}_3(\text{OH})(\text{H}_2\text{O})\text{Cl}_7$  is the building block in the polymeric anion in this complex.

2342

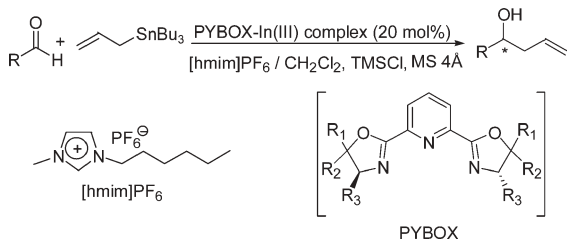


### Selective $\text{O}_2$ oxidation of air-sensitive lanthanocene thiolates and thioether chelate

Xigeng Zhou,\* Ming Zhu, Libei Zhang, Zhenyu Zhu, Chengfu Pi, Zhen Pang, Linhong Weng and Ruifang Cai

Two unprecedented selective  $\text{O}_2$  oxidation reactions of lanthanide-bound thiolates and a thioether chelate are established, demonstrating firstly that the  $\text{Ln-S}$  bond is more reactive to  $\text{O}_2$  than the  $\text{Ln-C}(\text{Cp})$  bond under the conditions involved and revealing a novel oxygenation pattern of thiolate ligands.

2345



### Enantioselective allylation of aldehydes catalyzed by chiral indium(III) complexes immobilized in ionic liquids

Jun Lu, Shun-Jun Ji\* and Teck-Peng Loh\*

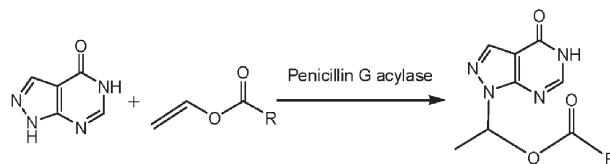
In the presence of chiral catalytic complexes prepared from  $\text{In}(\text{OTf})_3$  and chiral PYBOX ligands, allyltributylstannane reacted with aldehydes in ionic liquids to afford the corresponding homoallylic alcohols in high enantioselectivities (86–94% ee) and good yields (68–89%); the chiral catalysts immobilized in ionic liquids could be reused with comparable enantioselectivities and yields.

2348

**Penicillin G acylase catalyzed Markovnikov addition of allopurinol to vinyl ester**

Wei-Bo Wu, Na Wang, Jian-Ming Xu, Qi Wu and Xian-Fu Lin\*

A new enzymatic process is reported, in which penicillin G acylase from *Escherichia coli* displays a promiscuous activity in catalyzing the Markovnikov addition of allopurinol to vinyl ester.

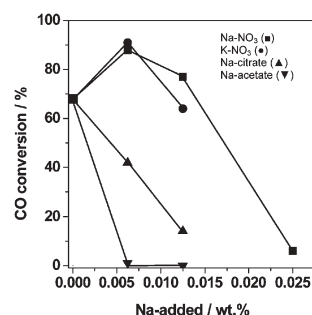


2351

**Unexpected promotion of Au/TiO<sub>2</sub> by nitrate for CO oxidation**

Benjamin Solsona, Marco Conte, Yu Cong, Albert Carley and Graham Hutchings\*

The catalytic activity for Au/TiO<sub>2</sub> for CO oxidation can be significantly enhanced by the addition of nitrates and this may relate to the variable catalyst performance observed in many studies.

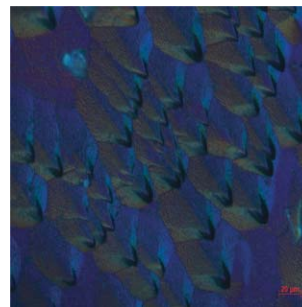


2354

**Phosphonate mediated surface reaction and reorganization: implications for the mechanism controlling cement hydration inhibition**

Corina Lupu, Rolf S. Arvidson, Andreas Lüttge\* and Andrew R. Barron\*

Vertical scanning interferometry provides an alternative mechanism for the length of time that a phosphonate hydration inhibitor will show efficacy: the rate of surface reorganization/restriction.

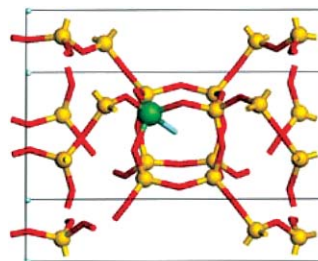


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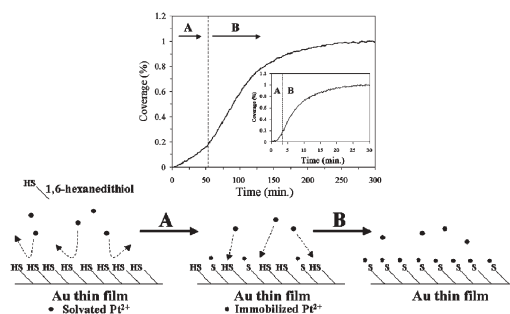
**Pentacoordinated germanium in AST zeolite synthesised in fluoride media. A <sup>19</sup>F NMR validated computational study**

German Sastre,\* Angeles Pulido and Avelino Corma

A computational study shows pentacoordinated Ge in the double four rings (D4R) of Si/Ge AST zeolites. The calculated chemical shifts of F-D4R containing 8Si, 7Si1Ge and 8Ge reproduce the trends of experimental <sup>19</sup>F NMR results.



2360

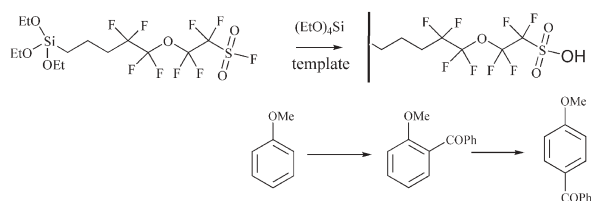


### Direct observation of a cooperative mechanism in the adsorption of heavy metal ions to thiolated surface by *in-situ* surface plasmon resonance measurements

Tae-wook Kang, Jung-woo Moon, Seogil Oh, Surin Hong, Soonwoo Chah and Jongheop Yi\*

S-type adsorption kinetics, obtained by surface plasmon resonance measurements, suggest that the rate of  $\text{Pt}^{2+}$  adsorption on 1,6-hexanedithiol (HDT) on Au increases until the surface coverage reaches *ca.* 17% (A), after which, the adsorption profile of  $\text{Pt}^{2+}$  follows Langmuirian behavior (B).

2363

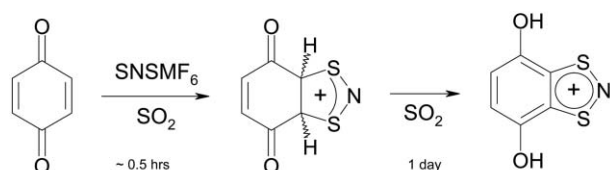


### Novel mesoporous silica–perfluorosulfonic acid hybrids as strong heterogeneous Brønsted catalysts

Duncan J. Macquarrie,\* Stewart J. Tavener and Mark A. Harmer

The sulfonic acid–mesoporous silica catalyst catalyses the acylation of anisole and the subsequent isomerisation of the *ortho* product very efficiently.

2366

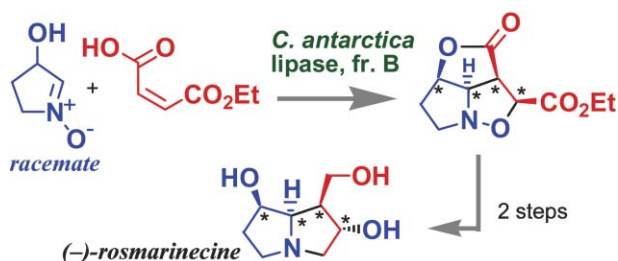


### Evolution of the pseudo-1,3-dipolar cycloaddition chemistry of $\text{SNSMF}_6$ ( $M = \text{As}, \text{Sb}$ ) leading to 2,5-dihydroxybenzo-1,3,2-dithiazolium and 2,7-dicarbonylnaphtha-1,3,2-dithiazolium salts and their corresponding radicals

Andreas Decken, Aaron Mailman, Saba M. Mattar and Jack Passmore\*

An unprecedented one-step synthesis of ring-fused 1,3,2-dithiazolium salts and their corresponding  $7\pi$  radicals provides a versatile template for designing a new class of radicals.

2369



### Lipase-catalyzed domino kinetic resolution of $\alpha$ -hydroxynitrones/intramolecular 1,3-dipolar cycloaddition: a concise asymmetric total synthesis of (–)-rosmarinic acid

Shuji Akai, Kouichi Tanimoto, Yukiko Kanao, Sohei Omura and Yasuyuki Kita\*

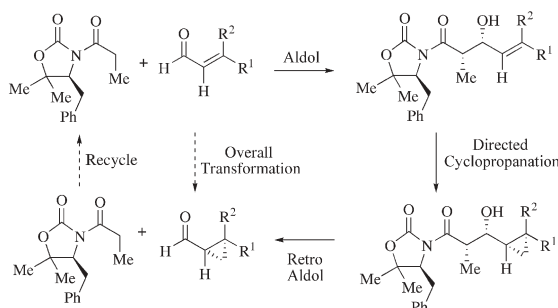
The title domino reactions were developed to directly provide tetrahydrofuro[3,4-*c*]isoxazole derivatives in  $\geq 90\%$  ee from racemic  $\alpha$ -hydroxynitrones, which were used in the concise asymmetric total synthesis of (–)-rosmarinic acid.

2372

### A novel strategy for the asymmetric synthesis of chiral cyclopropane carboxaldehydes

Matt Cheeseman, Fred J. P. Feuillet, Andrew L. Johnson and Steven D. Bull\*

A new strategy for combining chiral auxiliaries and substrate-directable reactions for asymmetric synthesis is described for a novel three-step protocol that employs a sequence of aldol–cyclopropanation–*retro*-aldol reactions for the stereoselective synthesis of enantiopure cyclopropane carboxaldehydes.

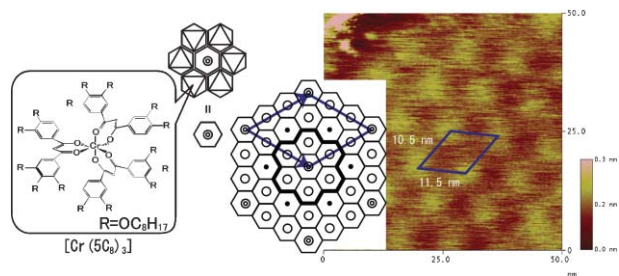


2375

### Nanometer-scale ordering in cast films of columnar metallomesogen as revealed by STM observations

Norishige Kakegawa,\* Naomi Hoshino, Yuki Matsuoka, Noboru Wakabayashi, Shin-ichiro Nishimura and Akihiko Yamagishi

STM observations were performed on a cast film of a columnar metallomesogen ( $[\text{Cr}(\text{5C}_8)_3]$ ) on a graphite surface, revealing the nanometer-scale surface ordering into an oblique lattice possibly due to the  $\Delta\Lambda$ -chiral interaction(s).

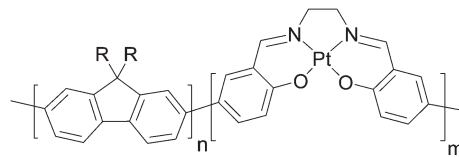


2378

### Semiconducting polyfluorenes with electrophosphorescent on-chain platinum–salen chromophores

Frank Galbrecht, Xiao Hui Yang, Benjamin S. Nehls, Dieter Neher, Tony Farrell and Ullrich Scherf\*

The synthesis of statistical fluorene-type copolymers with on-chain Pt–salen phosphorescent units and their use in electrophosphorescent OLEDs is reported.

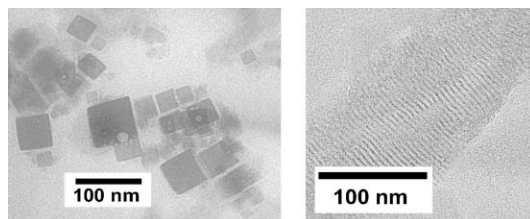


2381

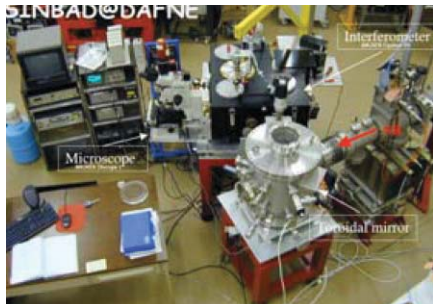
### Formation of $\text{GeO}_2$ nanosheets using water thin layers in lamellar phase as a confined reaction field—*in situ* measurement of SAXS by synchrotron radiation

Motonari Adachi,\* Keizo Nakagawa, Kensuke Sago, Yusuke Murata and Yukihiro Nishikawa

Crystallized layered  $\text{GeO}_2$  nanosheets were synthesized using a lamellar phase containing surfactant molecules at room temperature.



2384

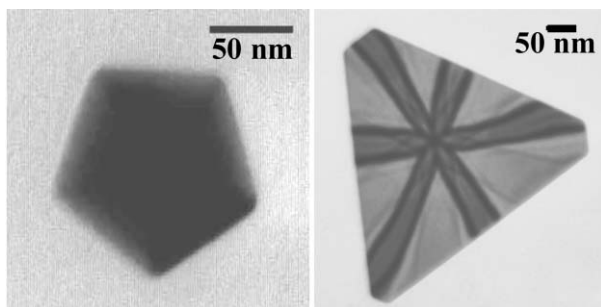


### Kinetics of polycondensation reactions during self-assembly of mesostructured films studied by *in situ* infrared spectroscopy

Plinio Innocenzi,\* Luca Malfatti, Tongjit Kidchob, Paolo Falcaro, Mariangela Cestelli Guidi, Massimo Piccinini and Augusto Marcelli

*In situ* synchrotron FTIR experiments have been performed during evaporation-induced self-assembly (EISA) of mesoporous films and the role of silica polycondensation in obtaining highly organized mesostructures has been illuminated.

2387

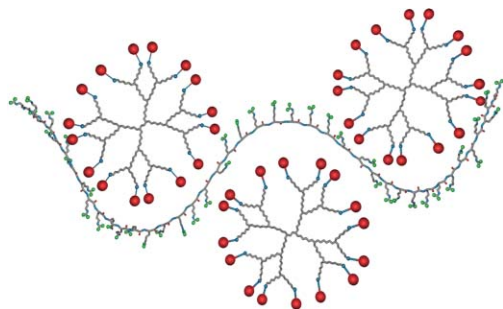


### Polygonal gold nanoplates in a polymer matrix

S. Porel, S. Singh and T. P. Radhakrishnan\*

Gold nanoplates are generated *in situ* in poly(vinyl alcohol) film, without any additional reducing agent, through mild thermal treatment. Polygonal geometries – pentagons, hexagons, triangles and squares/rectangles – are obtained depending on the composition and thermal treatment conditions.

2390

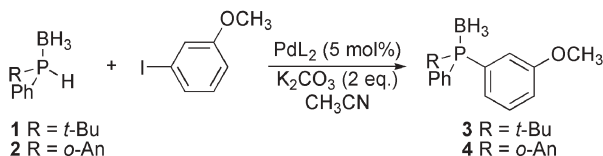


### Dendrimeric Gd(III) complex of a monophosphinated DOTA analogue: optimizing relaxivity by reducing internal motion†

Jakub Rudovský, Petr Hermann,\* Mauro Botta, Silvio Aime\* and Ivan Lukeš

A full-loaded G2-PAMAM conjugate with Gd(III) complexes showed remarkable enhancement of relaxivity upon addition of cationic polyaminoacids. This is ascribed to a “glue” effect arising from the interactions of the anionic complex moieties with the positively charged aminoacidic sidechains reducing the local internal mobility of the complexes.

2393



### Palladium catalysed enantioselective phosphination reactions using secondary phosphine-boranes and aryl iodide

Stéphanie Pican and Annie-Claude Gaumont\*

Enantioselective palladium-catalysed phosphination of an aryl iodide using an unhindered racemic secondary phosphine-borane gave *P*-stereogenic phosphine derivatives. The influence of the phosphorus substituent is crucial for the ee.

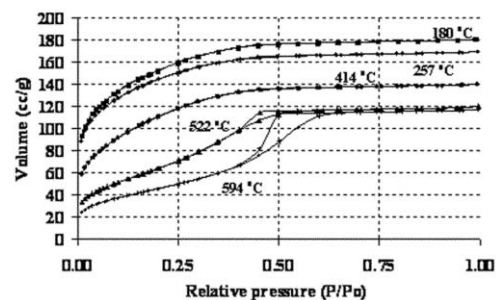


2396

### New families of supermicroporous metal oxides: the link between zeolites and mesoporous materials

Boris G. Shpeizer, Abraham Clearfield\* and Joy M. Heising

Sol-gel hydrolysis reactions in propanol of two or more metal acetates or alkoxides in *n*-alkylamines have been found to yield porous mixed oxides with the presence of pores largely in the 10–20 Å region.

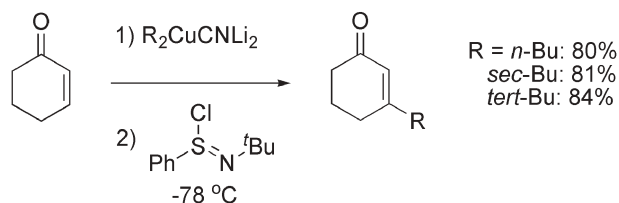


2399

### One-pot $\beta$ -substitution of enones with alkyl groups to $\beta$ -alkyl enones

Jun-ichi Matsuo\* and Yayoi Aizawa

One-pot  $\beta$ -substitution of enones with alkyl groups proceeded efficiently under mild conditions using  $R_2CuCNLi_2$  and  $PhS(Cl)=N^tBu$ .

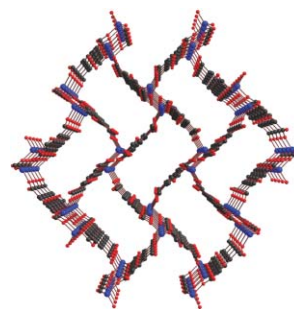


2402

### A three-dimensional porous metal-organic framework with the rutile topology constructed from triangular and distorted octahedral building blocks

Linhua Xie, Shuxia Liu,\* Bo Gao, Chundan Zhang, Chunyan Sun, Dehui Li and Zhongmin Su

The solvothermal reaction of zinc acetate dihydrate with 1,3,5-benzenetricarboxylic acid yields a three-dimensional porous metal-organic framework constructed from triangular and distorted octahedral building blocks, the framework of which can be described as a decorated rutile net.

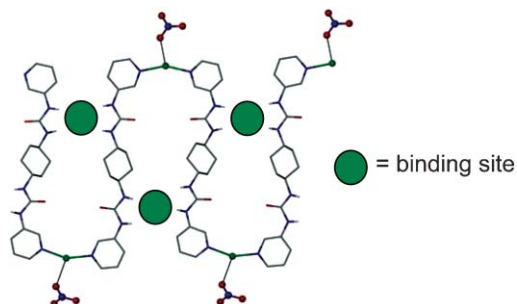


2405

### Influence of hydrogen bonding on coordination polymer assembly

Lucas Applegarth, Andres E. Goeta and Jonathan W. Steed\*

The conformation of an  $Ag(I)$  coordination polymer is controlled by peripheral hydrogen bonding to anions and neutral molecules to give either a sandwich structure (DMSO guest) or an open chain (nitrate guest).




## AUTHOR INDEX

- Adachi, Motonari, 2381  
Aida, Takuzo, 2324  
Aime, Silvio, 2390  
Aizawa, Yayoi, 2399  
Akai, Shuji, 2369  
Appelgarth, Lucas, 2405  
Arvidson, Rolf S., 2354  
Barron, Andrew R., 2354  
Botta, Mauro, 2390  
Bull, Steven D., 2372  
Cai, Ruifang, 2342  
Carley, Albert, 2351  
Chah, Soonwoo, 2360  
Cheeseman, Matt, 2372  
Chikaraishi, Midori, 2321  
Chivers, Tristram, 2339  
Clearfield, Abraham, 2396  
Cong, Yu, 2351  
Conte, Marco, 2351  
Corma, Avelino, 2357  
Davies, Paul W., 2307  
Decken, Andreas, 2366  
Falcaro, Paolo, 2384  
Fan, Jian, 2327  
Farrell, Tony, 2378  
Feuillet, Fred J. P., 2372  
Fu, Zhiyong, 2339  
Fukazawa, Yoshimasa, 2321  
Fürstner, Alois, 2307  
Galbrecht, Frank, 2378  
Gao, Bo, 2402  
Gao, Song, 2336  
Gaumont, Annie-Claude, 2393  
Goeta, Andres E., 2405  
Grochala, Wojciech, 2330  
Guidi, Mariangela Cestelli, 2384  
Haino, Takeharu, 2321  
Hanson, Brian E., 2327  
Harmer, Mark A., 2363  
Heising, Joy M., 2396  
Hermann, Petr, 2390  
Hong, Surin, 2360  
Hoshino, Naomi, 2375  
Hutchings, Graham, 2351  
Innocenzi, Plinio, 2384  
Ji, Shun-Jun, 2345  
Johnson, Andrew L., 2372  
Kakegawa, Norishige, 2375  
Kanao, Yukiko, 2369  
Kang, Taewook, 2360  
Kidchob, Tongjit, 2384  
Kita, Yasuyuki, 2369  
Kobayashi, Mutsumi, 2321  
Li, Baolong, 2333  
Li, Baozong, 2333  
Li, Dehui, 2402  
Lin, Xian-Fu, 2348  
Liu, Shuxia, 2402  
Loh, Teck-Peng, 2345  
Lu, Jun, 2345  
Lukeš, Ivan, 2390  
Lupu, Corina, 2354  
Lüttge, Andreas, 2354  
Ma, Bao-Qing, 2336  
Macquarrie, Duncan J., 2363  
Mailman, Aaron, 2366  
Malfatti, Luca, 2384  
Marcelli, Augusto, 2384  
Matsuo, Jun-ichi, 2399  
Matsuoka, Yuki, 2375  
Mattar, Saba M., 2366  
Moon, Jungwoo, 2360  
Murata, Yusuke, 2381  
Nakagawa, Keizo, 2381  
Neher, Dieter, 2378  
Nehls, Benjamin S., 2378  
Nishikawa, Yukihiko, 2381  
Nishimura, Shin-ichiro, 2375  
Oh, Seogil, 2360  
Omura, Sohei, 2369  
Osuka, Atsuhiko, 2324  
Pang, Zhen, 2342  
Passmore, Jack, 2366  
Peng, Yanfen, 2333  
Pi, Chengfu, 2342  
Pican, Stéphanie, 2393  
Piccini, Massimo, 2384  
Porel, S., 2387  
Pulido, Angeles, 2357  
Radhakrishnan, T. P., 2387  
Rudovský, Jakub, 2390  
Sago, Kensuke, 2381  
Sastre, German, 2357  
Sato, Hiroshi, 2324  
Scherf, Ullrich, 2378  
Shinmori, Hideyuki, 2324  
Shpeizer, Boris G., 2396  
Singh, S., 2387  
Solsona, Benjamin, 2351  
Steed, Jonathan W., 2405  
Su, Zhongmin, 2402  
Sun, Chunyan, 2402  
Sun, Hao-Ling, 2336  
Tanimoto, Kouichi, 2369  
Tashiro, Kentaro, 2324  
Tavener, Stewart J., 2363  
Thompson, Laurence K., 2339  
Wakabayashi, Noboru, 2375  
Wang, Na, 2348  
Weng, Linhong, 2342  
Wu, Qi, 2348  
Wu, Wei-Bo, 2348  
Xie, Linhua, 2402  
Xu, Jian-Ming, 2348  
Yamagishi, Akihiko, 2375  
Yang, Xiao Hui, 2378  
Yi, Jongheop, 2360  
Zhang, Chundan, 2402  
Zhang, Libei, 2342  
Zhang, Yong, 2333  
Zhou, Xigeng, 2342  
Zhu, Ming, 2342  
Zhu, Zhenyu, 2342

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