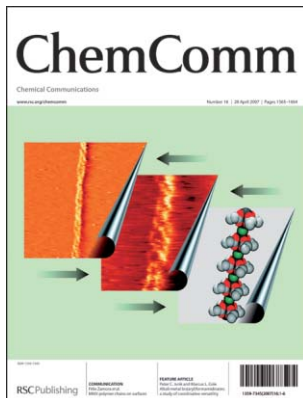


## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (16) 1565-1664 (2007)



### Cover

See Félix Zamora *et al.*, page 1591. The image shows a nanometric chain of an MMX polymer isolated on an HOPG surface, showing a helical internal structure. Image reproduced by permission of David Olea, Rodrigo González-Prieto, José L. Priego, M. Carmen Barral, Pedro J. de Pablo, M. Rosario Torres, Julio Gómez-Herrero, Reyes Jiménez-Aparicio and Félix Zamora, from *Chem. Commun.*, 2007, 1591.

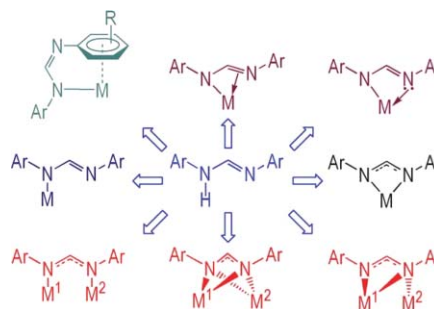
## FEATURE ARTICLE

1579

### Alkali-metal bis(aryl)formamidinates: a study of coordinative versatility

Peter C. Junk and Marcus L. Cole

This article highlights the coordinative versatility of one alkali-metal amidinate subclass; the bis(aryl)formamidinates. These compounds are invaluable in transition-metal studies but until recently had not been investigated in their own right.



## COMMUNICATIONS

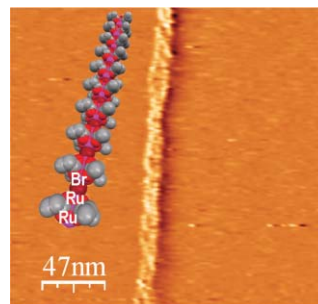
1591



### MMX polymer chains on surfaces

David Olea, Rodrigo González-Prieto, José L. Priego, M. Carmen Barral, Pedro J. de Pablo, M. Rosario Torres, Julio Gómez-Herrero,\* Reyes Jiménez-Aparicio\* and Félix Zamora\*

Fibres of a MMX polymer chain have been isolated on different surfaces showing an unexpected helical internal structure.



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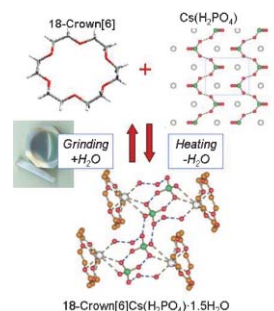
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1594

**Reversible solid-state reaction between 18-Crown[6] and  $M[H_2PO_4]$  ( $M = K, Rb, Cs$ ) and an investigation of the decomplexation process**

Dario Braga,\* Marco Polito, Elena Dichiarante, Katia Rubini and Fabrizia Grepioni\*

Thermal dehydration of solid 18-Crown[6]· $M[H_2PO_4]$ · $xH_2O$  ( $x = 2$  for  $M = K, Rb$ ;  $x = 1.5$  for  $M = Cs$ ), prepared by mechanical mixing of 18-Crown[6] and  $M[H_2PO_4]$ , is accompanied by *extrusion* of the crown ether and reconstruction of  $M[H_2PO_4]$ . The mixture reverts to the starting complex upon grinding in air.

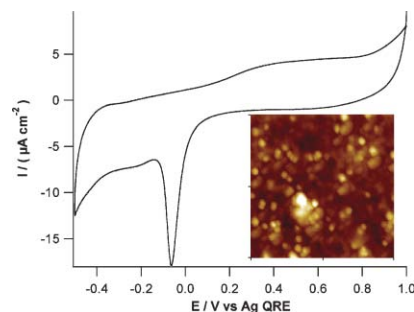


1597

**Formation and evaluation of electrochemically-active ultra-thin palladium–Nafion nanocomposite films**

Paolo Bertoncello,\* Massimo Peruffo and Patrick R. Unwin\*

A simple method for producing electrochemically-active palladium nanoparticles within ultra-thin Nafion films is described.

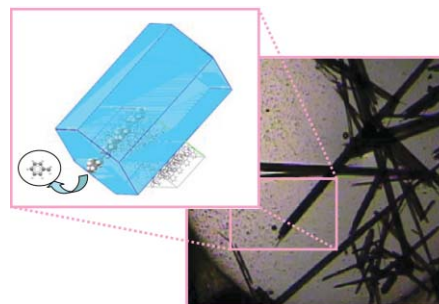


1600

**Solvent inclusion in form II carbamazepine**

Aurora J. Cruz Cabeza, Graeme M. Day, W. D. Samuel Motherwell and William Jones\*

Experimental and theoretical evidence of solvent inclusion in form II carbamazepine is presented in this study. Once the inclusion properties were established, a long chain hydrocarbon was included in the crystal form leading to an isomorphous pseudopolymorph with improved physical stability.

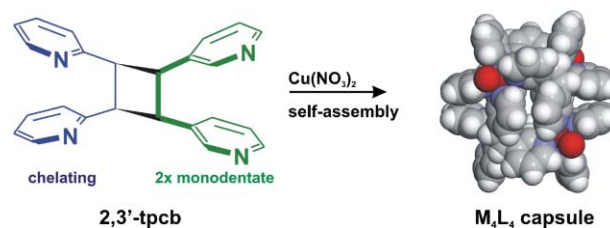


1603

**Coding a coordination-driven self-assembly via a hydrogen bond-directed solid-state synthesis: An unexpected chiral tetrahedral capsule**

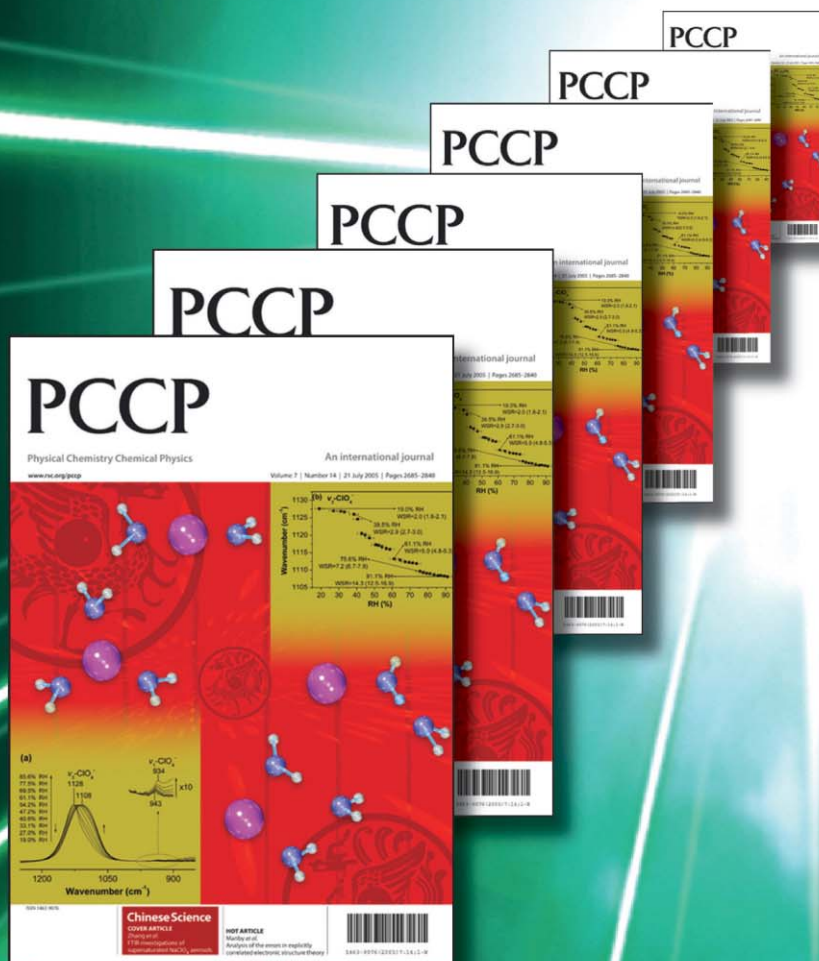
Tamara D. Hamilton, Dejan-Krešimir Bučar and Leonard R. MacGillivray\*

A hydrogen bond-directed organic synthesis has been used to code the formation of a chiral tetrahedral  $M_4L_4$  capsule.





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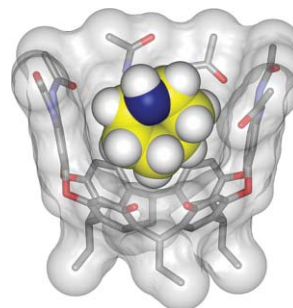
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1605

### A cavitand stabilizes the Meisenheimer complex of $S_NAr$ reactions

Sara M. Butterfield and Julius Rebek, Jr.\*

A deep cavitand binds amine nucleophiles and accelerates their subsequent  $S_NAr$  reactions by solvating the intermediate Meisenheimer complex.

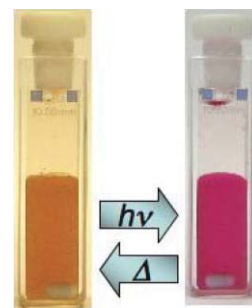


1608

### Photochromism of 7-(*N,N*-diethylamino)-4'-hydroxyflavylium in a water–ionic liquid biphasic system

Fernando Pina,\* A. Jorge Parola, Maria João Melo, César A. T. Laia and Carlos A. M. Afonso

Photochromism of *trans*-4-(*N,N*-diethylamino)-2,4'-dihydroxychalcone, with formation of the photoproduct 7-(*N,N*-diethylamino)-4'-hydroxyflavylium, is promoted in the ionic liquid phase of a water/[bmim][PF<sub>6</sub>] biphasic system.

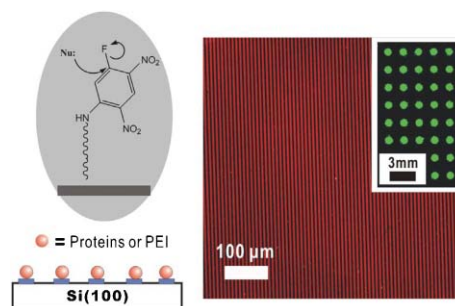


1611

### Photoreactive immobilization of 11-(2,4-dinitro-5-fluorobenzene)undecenamide on a hydrogenated silicon (100) surface for protein immobilizations

Tai Hwan Ha,\* Mi-ra Park, Hye Jung Park, Jae-Sik Choi, Guncheol Kim,\* Moon Seop Hyun and Bong Hyun Chung\*

Several nucleophiles such as proteins or poly(ethyleneimine) could be easily conjugated with a 11-(2,4-dinitro-5-fluorobenzene)undecenamide (DFUA) monolayer photochemically prepared on a silicon (100) surface.

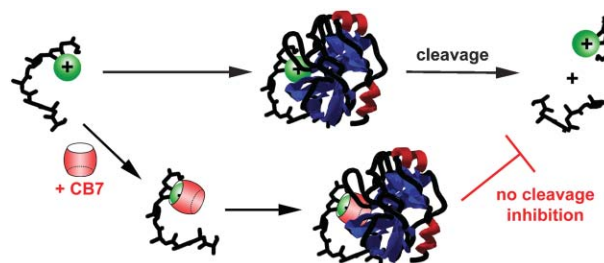


1614

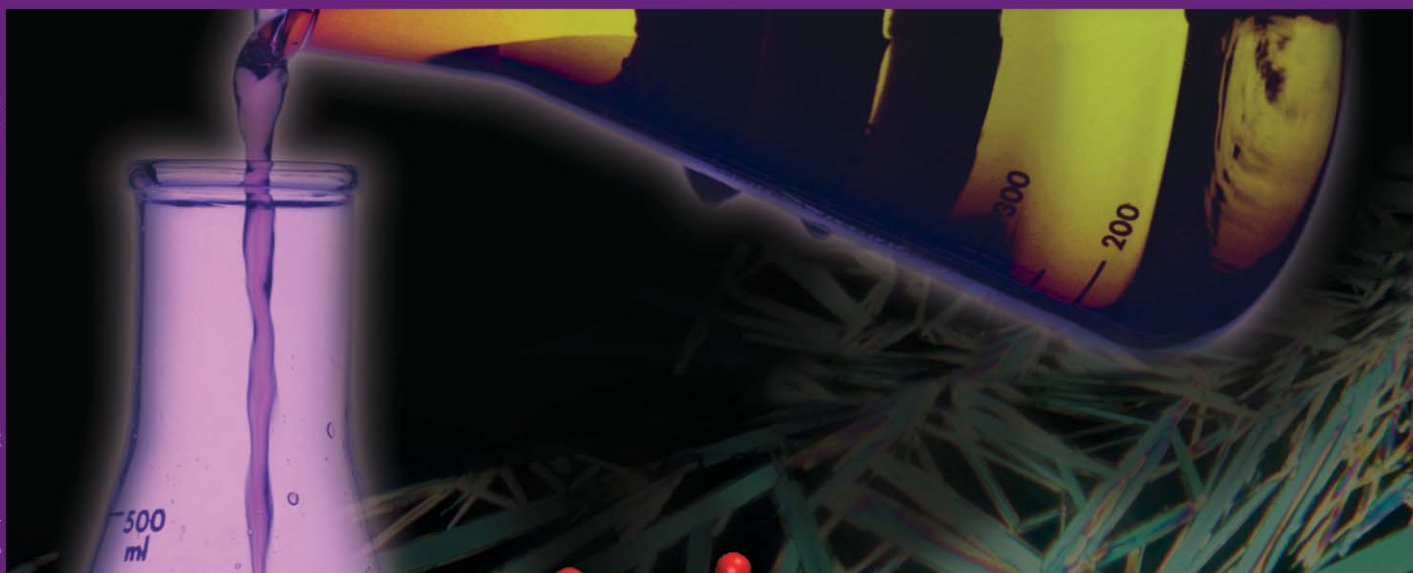
### Effects of cucurbit[7]uril on enzymatic activity

Andreas Hennig, Garima Ghale and Werner M. Nau\*

The macrocyclic host cucurbit[7]uril exhibits highly specific inhibitory effects on the activity of proteases, which can be analyzed by a host-substrate complexation model. A preferential stabilization of substrates with cationic recognition sites was observed.





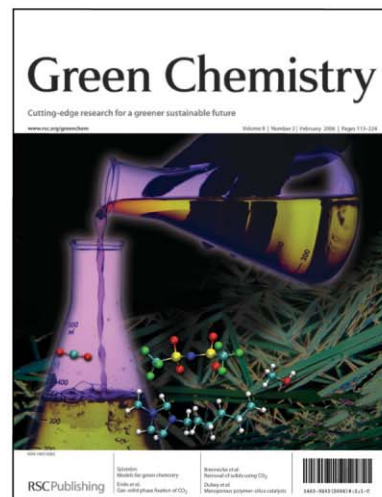


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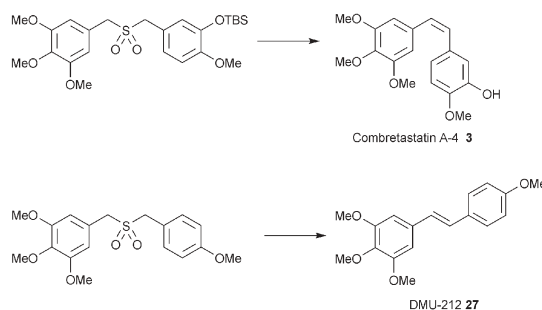


1617

### A Ramberg–Bäcklund route to the stilbenoid anti-cancer agents combretastatin A-4 and DMU-212

James E. Robinson and Richard J. K. Taylor\*

A concise route to combretastatin A-4 using a Ramberg–Bäcklund reaction to form the key (*Z*)-stilbene unit has been developed. This approach has been extended to prepare the (*E*)-stilbene DMU-212.

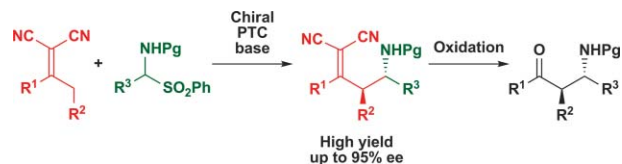


1620

### The asymmetric vinylogous Mannich reaction of dicyanoalkylidenes with $\alpha$ -amido sulfones under phase-transfer conditions

Barbara Niess and Karl Anker Jørgensen\*

The stereoselective vinylogous Mannich reaction of dicyanoalkylidenes under phase-transfer catalytic conditions utilizing stable  $\alpha$ -amido sulfones as imine precursors is presented.

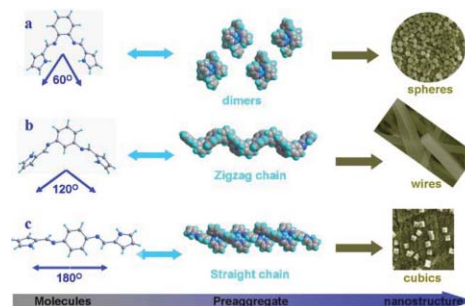


1623

### Distinct nanostructures from isomeric molecules of bis(iminopyrrole) benzenes: effects of molecular structures on nanostructural morphologies

Yaobing Wang, Hongbing Fu,\* Aidong Peng, Yongsheng Zhao, Jinshi Ma, Ying Ma and Jiannian Yao\*

The effects of molecular structures on nanostructural morphologies have been studied through the preparation of nanospheres, square nanowires and nanocubes from three isomeric molecules of bis(iminopyrrole)benzene.

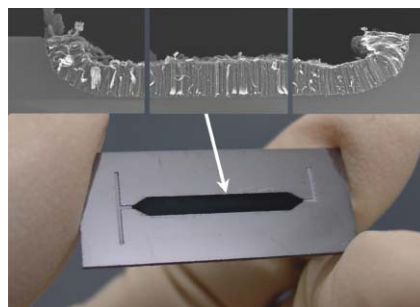


1626

### Microreactor utilizing a vertically-aligned carbon nanotube array grown inside the channels

Naoki Ishigami, Hiroki Ago,\* Yukihiro Motoyama, Mikihiro Takasaki, Masashi Shinagawa, Kohji Takahashi, Tatsuya Ikuta and Masaharu Tsuji

A new type of microreactor incorporating a vertically-aligned carbon nanotube array in the reaction channels was fabricated, which showed much higher catalytic activity and longer lifetime as compared with conventional microreactors.





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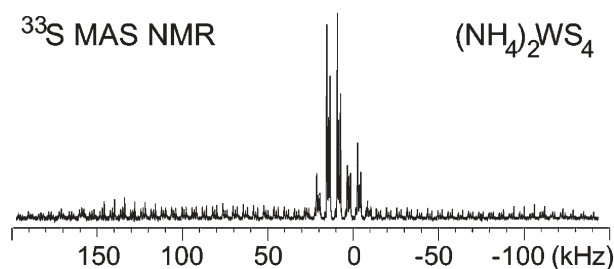


1629

**Advancements in natural abundance solid-state  $^{33}\text{S}$  MAS NMR: characterization of transition-metal M=S bonds in ammonium tetrathiomallates**

Hans J. Jakobsen,\* Anders R. Hove, Henrik Bildsøe, Jørgen Skibsted and Michael Brorson

Detection of  $^{33}\text{S}$  satellite transitions in natural abundance  $^{33}\text{S}$  MAS NMR has allowed determination of both  $^{33}\text{S}$  chemical shift anisotropy and quadrupole coupling parameters for the tetrathiomallates  $(\text{NH}_4)_2\text{MS}_4$  (M = Mo and W).

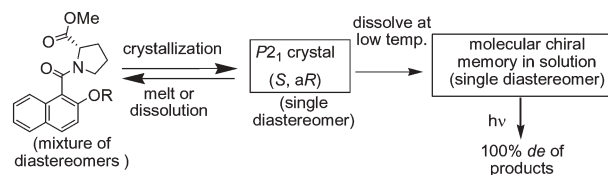


1632

**Diastereoselective photocycloaddition using memory effect of molecular chirality controlled by crystallization**

Masami Sakamoto,\* Atsushi Unosawa, Shuichiro Kobaru, Yasuhiro Hasegawa, Takashi Mino, Yoshio Kasashima and Tsutomu Fujita

Naphthamides derived from L-proline, which exist as a mixture of several diastereomers in solution, converged to single diastereomer by crystallization, and the conformational transformation was controlled after the crystals were dissolved in the solvent at low temperature.

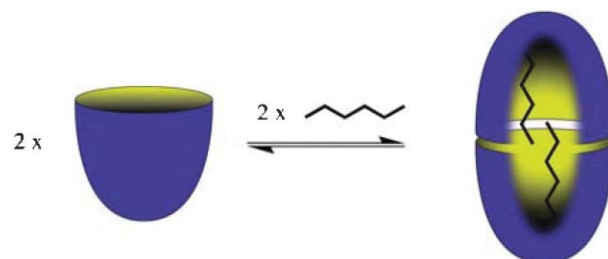


1635

**Straight-chain alkanes template the assembly of water-soluble nano-capsules**

Corinne L. D. Gibb and Bruce C. Gibb\*

Small alkanes such as hexane form capsular, quaternary complexes with a water-soluble cavitanid, while larger guest such as heptadecane form ternary (2 : 1) capsular complexes. Guests are tightly packed in the latter, reminiscent of the internal environment of proteins.

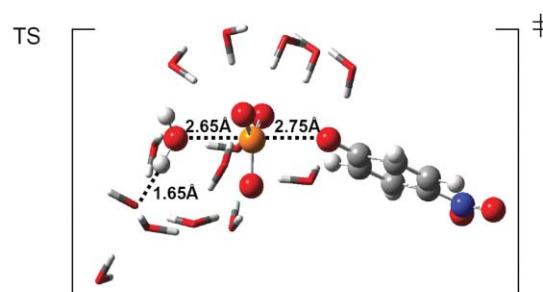


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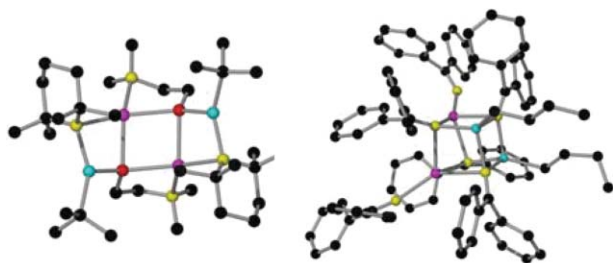
**Supramolecule density functional calculations suggest a key role for solvent in alkaline hydrolysis of *p*-nitrophenyl phosphate**

Lidong Zhang, Daiqian Xie,\* Dingguo Xu and Hua Guo\*

Supramolecule density functional theory calculations show that solvent is responsible for the concerted transition state in alkaline hydrolysis of *p*-nitrophenyl phosphate suggested by heavy atom kinetic isotope effects.



1641

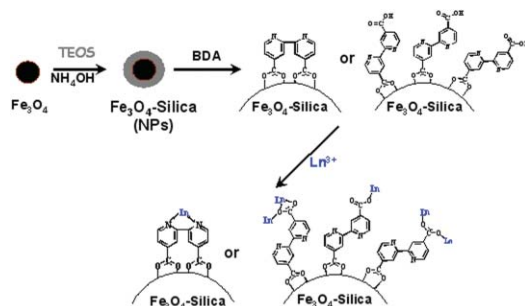


**Structural variations in bimetallic sodium–magnesium and sodium–zinc ketimides, and a sodium–zinc alkide–alkoxide–amide: connections to ring-stacking, ring-laddering, and inverse crown concepts**

William Clegg, Sophie H. Dale, David V. Graham, Ross W. Harrington, Eva Hevia, Lorna M. Hogg, Alan R. Kennedy and Robert E. Mulvey\*

Stacks and ladders, classical structural motifs in organolithium chemistry, have also been found in mixed sodium–zinc heterobianionic and heterotri-anionic complexes.

1644

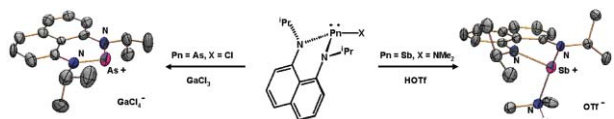


**Fabrication of silica-coated magnetic nanoparticles with highly photoluminescent lanthanide probes**

Jungkweon Choi, Jin Chul Kim, Yong Bok Lee, In Seon Kim, Yong Ki Park and Nam Hwi Hur\*

The biocompatible luminescent–magnetic NPs composed of lanthanide ions as luminescent markers with silica-coated magnetic NPs as cores show a significantly enhanced luminescence due to the ligand-to-metal energy transfer.

1647

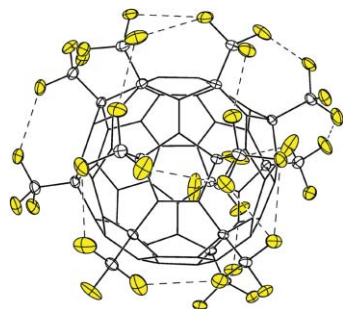


**Diamidonaphthalene-supported pnictogenium cations: Synthesis of an N-heterocyclic stibonium cation by a novel protonation route**

Heather A. Spinney, Iliia Korobkov and Darrin S. Richeson\*

Diamidonaphthalene provides a unique stabilizing framework for the construction of N-heterocyclic arsenium and stibonium cations, which, in the case of the Sb cation, involved a novel synthetic route based on ligand protonation.

1650



**X-ray structure and DFT study of  $C_1$ - $C_{60}(\text{CF}_3)_{12}$ . A high-energy, kinetically-stable isomer prepared at 500 °C**

Ivan E. Kareev, Natalia B. Shustova, Dmitry V. Peryshkov, Sergey F. Lebedkin, Susie M. Miller, Oren P. Anderson, Alexey A. Popov,\* Olga V. Boltalina\* and Steven H. Strauss\*

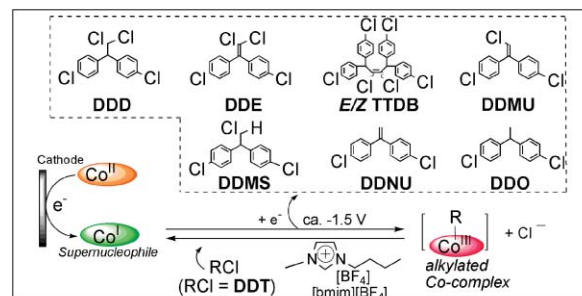
This asymmetric isomer of  $C_{60}(\text{CF}_3)_{12}$ , prepared at 500 °C, has an unprecedented addition pattern that is 40 kJ mol<sup>-1</sup> less stable than the previously reported isomer of  $C_{60}(\text{CF}_3)_{12}$ .

1653

### Enhanced reactivity of hydrophobic vitamin B<sub>12</sub> towards the dechlorination of DDT in ionic liquid

Md. Abdul Jabbar, Hisashi Shimakoshi and Yoshio Hisaeda\*

The electrolytic dechlorination of DDT and DDD with a cobalamin derivative in ionic liquid provided enhanced reactivity, and the recyclability of the catalyst is useful for developing “green” technologies.

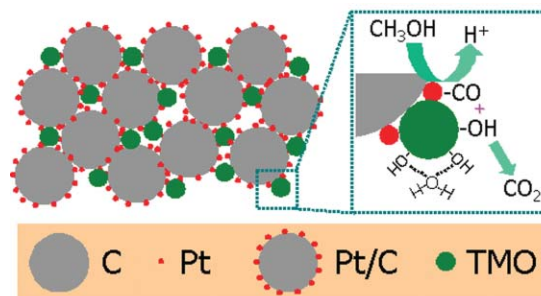


1656

### Facile approach to enhance the Pt utilization and CO-tolerance of Pt/C catalysts by physically mixing with transition-metal oxide nanoparticles

Jingyu Xi, Jianshe Wang, Lihong Yu, Xinping Qiu\* and Liquan Chen

A promising method to design the anode catalyst architecture for DAFCs by physically mixing Pt/C catalyst with transition-metal oxide nanoparticles is presented and electrochemical measurements confirm that this unique catalyst structure has excellent activity toward alcohol and CO electro-oxidation.

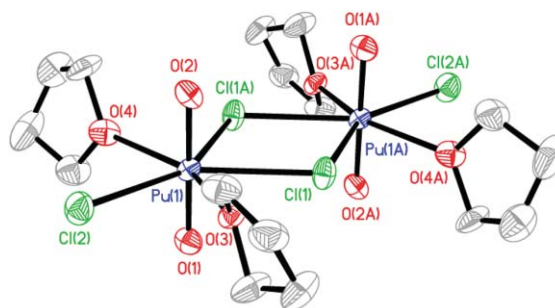


1659

### An entry route into non-aqueous plutonyl coordination chemistry

Andrew J. Gaunt,\* Sean D. Reilly, Trevor W. Hayton, Brian L. Scott and Mary P. Neu\*

The Pu(VI) dimer  $[\text{PuO}_2\text{Cl}_2(\text{thf})_2]_2$  (**1**), was synthesized and characterized by dissolution of a thf suspension of  $\text{PuO}_2\text{CO}_3$  by a solution of HCl in  $\text{Et}_2\text{O}$ ; the isolated complex (**1**) allows unprecedented access for the exploration of non-aqueous plutonyl coordination chemistry under inert atmospheric environments.



## ADDITION AND CORRECTION

1662

### Photoinduced electron transfer in a Watson–Crick base-paired, 2-aminopurine:uracil- $\text{C}_{60}$ hydrogen bonding conjugate

Francis D'Souza, Suresh Gadde, D.-M. Shafiqul Islam, Siew-Cheng Pang, Amy Lea Schumacher, Melvin E. Zandler, Rumiko Horie, Yasuyuki Araki and Osamu Ito




## AUTHOR INDEX

- Afonso, Carlos A. M., 1608  
Ago, Hiroki, 1626  
Anderson, Oren P., 1650  
Barral, M. Carmen, 1591  
Bertoncello, Paolo, 1597  
Bildsøe, Henrik, 1629  
Boltalina, Olga V., 1650  
Braga, Dario, 1594  
Brorson, Michael, 1629  
Bučar, Dejan-Krešimir, 1603  
Butterfield, Sara M., 1605  
Chen, Liquan, 1656  
Choi, Jae-Sik, 1611  
Choi, Jungkweon, 1644  
Chung, Bong Hyun, 1611  
Clegg, William, 1641  
Cole, Marcus L., 1579  
Cruz Cabeza, Aurora J., 1600  
Dale, Sophie H., 1641  
Day, Graeme M., 1600  
de Pablo, Pedro J., 1591  
Dichiarante, Elena, 1594  
Fu, Hongbing, 1623  
Fujita, Tsutomu, 1632  
Gaunt, Andrew J., 1659  
Ghale, Garima, 1614  
Gibb, Bruce C., 1635  
Gibb, Corinne L. D., 1635  
Gómez-Herrero, Julio, 1591  
González-Prieto, Rodrigo, 1591  
Graham, David V., 1641  
Grepioni, Fabrizia, 1594  
Guo, Hua, 1638  
Ha, Tai Hwan, 1611  
Hamilton, Tamara D., 1603  
Harrington, Ross W., 1641  
Hasegawa, Yasuhiro, 1632  
Hayton, Trevor W., 1659  
Hennig, Andreas, 1614  
Hevia, Eva, 1641  
Hisaeda, Yoshio, 1653  
Hogg, Lorna M., 1641  
Hove, Anders R., 1629  
Hur, Nam Hwi, 1644  
Hyun, Moon Seop, 1611  
Ikuta, Tatsuya, 1626  
Ishigami, Naoki, 1626  
Jabbar, Md. Abdul, 1653  
Jakobsen, Hans J., 1629  
Jiménez-Aparicio, Reyes, 1591  
Jones, William, 1600  
Jørgensen, Karl Anker, 1620  
Junk, Peter C., 1579  
Kareev, Ivan E., 1650  
Kasashima, Yoshio, 1632  
Kennedy, Alan R., 1641  
Kim, Guncheol, 1611  
Kim, In Seon, 1644  
Kim, Jin Chul, 1644  
Kobaru, Shuichiro, 1632  
Korobkov, Ilia, 1647  
Laia, César A. T., 1608  
Lebedkin, Sergey F., 1650  
Lee, Yong Bok, 1644  
Ma, Jinshi, 1623  
Ma, Ying, 1623  
MacGillivray, Leonard R., 1603  
Melo, Maria João, 1608  
Miller, Susie M., 1650  
Mino, Takashi, 1632  
Motherwell, W. D. Samuel, 1600  
Motoyama, Yukihiro, 1626  
Mulvey, Robert E., 1641  
Nau, Werner M., 1614  
Neu, Mary P., 1659  
Niess, Barbara, 1620  
Olea, David, 1591  
Park, Hye Jung, 1611  
Park, Mi-ra, 1611  
Park, Yong Ki, 1644  
Parola, A. Jorge, 1608  
Peng, Aidong, 1623  
Peruffo, Massimo, 1597  
Peryshkov, Dmitry V., 1650  
Pina, Fernando, 1608  
Polito, Marco, 1594  
Popov, Alexey A., 1650  
Priego, José L., 1591  
Qiu, Xinpings, 1656  
Rebek, Jr., Julius, 1605  
Reilly, Sean D., 1659  
Richeson, Darrin S., 1647  
Robinson, James E., 1617  
Rubini, Katia, 1594  
Sakamoto, Masami, 1632  
Scott, Brian L., 1659  
Shimakoshi, Hisashi, 1653  
Shinagawa, Masashi, 1626  
Shustova, Natalia B., 1650  
Skibsted, Jørgen, 1629  
Spinney, Heather A., 1647  
Strauss, Steven H., 1650  
Takahashi, Kohji, 1626  
Takasaki, Mikihiro, 1626  
Taylor, Richard J. K., 1617  
Torres, M. Rosario, 1591  
Tsuji, Masaharu, 1626  
Unosawa, Atsushi, 1632  
Unwin, Patrick R., 1597  
Wang, Jianshe, 1656  
Wang, Yaobing, 1623  
Xi, Jingyu, 1656  
Xie, Daiqian, 1638  
Xu, Dingguo, 1638  
Yao, Jiannian, 1623  
Yu, Lihong, 1656  
Zamora, Félix, 1591  
Zhang, Lidong, 1638  
Zhao, Yongsheng, 1623

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