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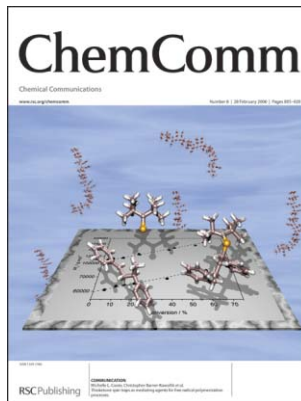
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (8) 805-920 (2006)



Cover

See Hiromichi Fujioka, Yasuyuki Kita *et al.*, page 832. Asymmetric discrimination of cyclohexa-2,5-dienyl-1-methylaldehyde with 1,2-diaryl-1,2-diamine gave a tetrahydroindoline analogue. Image reproduced by permission of Hiromichi Fujioka, Kenchi Murai, Yusuke Ohba, Hideki Hirose and Yasuyuki Kita from *Chem. Commun.*, 2006, 832.



Inside cover

See Michelle L. Coote, Christopher Barner-Kowollik *et al.*, page 835. Thioketones are suitable agents for controlling free radical polymerization processes: the polymerizations carry living characteristics induced by a persistent radical effect. Image reproduced by permission of Andrew Ah Toy, Hugh Chaffey-Millar, Thomas P. Davis, Martina H. Stenzel, Ekaterina I. Izgorodina, Michelle L. Coote and Christopher Barner-Kowollik from *Chem. Commun.*, 2006, 835.

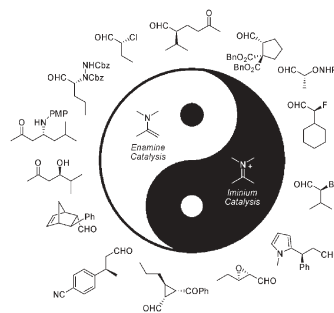
40TH ANNIVERSARY ARTICLE

819

The ying and yang of asymmetric aminocatalysis

Benjamin List

During the last six years the asymmetric catalysis of carbonyl transformations *via* iminium ion and enamine intermediates using chiral amines as organocatalysts has grown most remarkably. In this personal account an overview of this area is given.



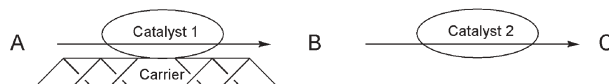
FEATURE ARTICLE

825

Carrier enabled catalytic reaction cascades

Lars Veum and Ulf Hanefeld*

Catalytic reaction cascades are often hampered by undesired interactions between the different reaction components. Carriers can play a crucial role in circumventing these problems.



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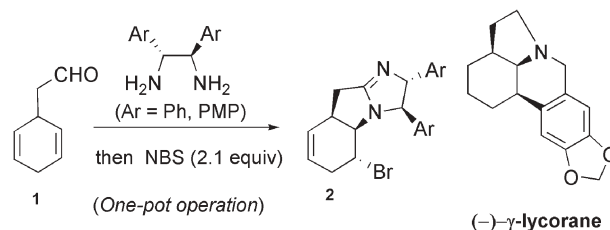
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Intramolecular bromo-amination of 1,4-cyclohexadiene aminal: one-pot discrimination of two olefins and concise asymmetric synthesis of (-)- γ -lycorane

Hiromichi Fujioka,* Kenichi Murai, Yusuke Ohba, Hideki Hirose and Yasuyuki Kita*

One-pot transformation of 1,4-cyclohexadiene aldehyde **1** to the optically active tetrahydroindoline analogue **2** was achieved using chiral 1,2-diamines. The method was applied for the concise asymmetric synthesis of (-)- γ -lycorane.

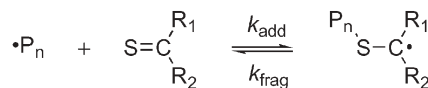


835

Thioketone spin traps as mediating agents for free radical polymerization processes

Andrew Ah Toy, Hugh Chaffey-Millar, Thomas P. Davis, Martina H. Stenzel, Ekaterina I. Izgorodina, Michelle L. Coote* and Christopher Barner-Kowollik*

Thioketones are demonstrated to be suitable agents for controlling free radical polymerization processes: the polymerizations carry (pseudo) living characteristics indicating that the control process is induced by a persistent radical effect.

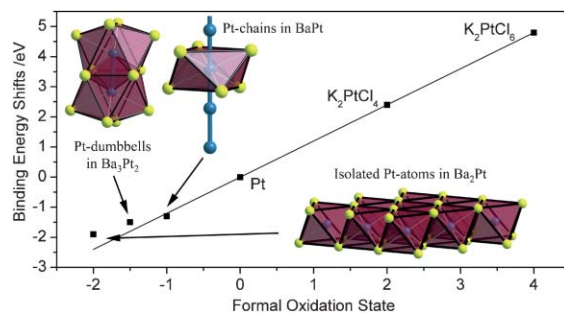


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An experimental proof for negative oxidation states of platinum: ESCA-measurements on barium platinides

Andrey Karpov, Mitsuharu Konuma and Martin Jansen*

ESCA-measurements on barium platinides provide the first spectroscopic evidence for negative oxidation states of platinum and are in excellent agreement with theoretical predictions based on quantum-chemical calculations.

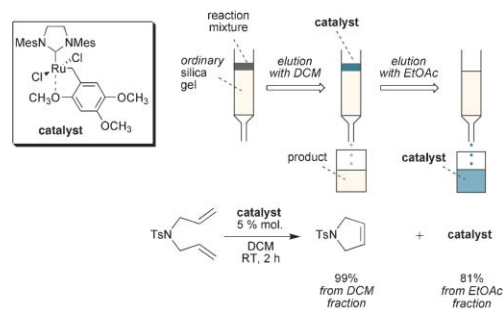


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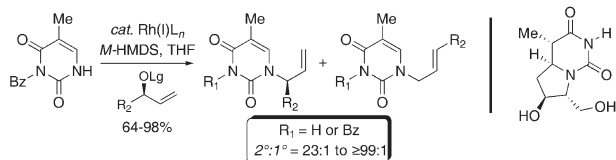
A simple and practical phase-separation approach to the recycling of a homogeneous metathesis catalyst

Anna Michrowska, Łukasz Gułajski and Karol Grela*

The air stable asarone-derived Ru carbene **16**, a robust olefin metathesis catalyst, can be easily separated after reaction by deposition on silica gel and reused up to nine times. This procedure provides products of excellent purity with low Ru content. This process can be automated and has been successfully applied to very small scale reactions. It therefore may be found useful for preparing small quantities of pure compound for biological screening.



844

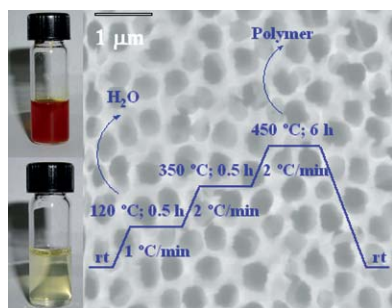


Regioselective and enantiospecific rhodium-catalyzed allylic amination with thymine: synthesis of a new conformationally rigid nucleoside

P. Andrew Evans,* Kwong Wah Lai, Hai-Ren Zhang and John C. Huffman

The regioselective and enantiospecific rhodium-catalyzed allylic amination of secondary allylic carbonates with *N*³-benzoyl thymine in conjunction with a stereoselective free radical cyclization provides a convenient method for the construction of a new conformationally rigid nucleoside.

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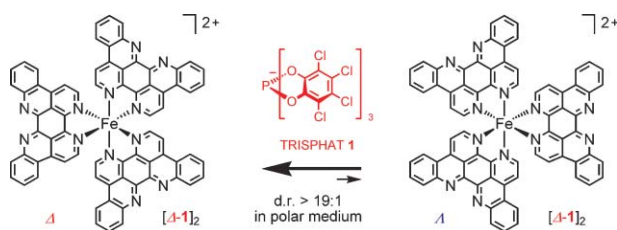


Conformal coating of nanoscale features of microporous Anodisc™ membranes with zirconium and titanium oxides

Piyush Shukla, Edel M. Minogue, T. Mark McCleskey, Q. X. Jia, Yuan Lin, Ping Lu and Anthony K. Burrell*

We report on a new solution technique known as Polymer Assisted Deposition (PAD) and its ability to conformally coat porous materials with 200 nm openings.

850

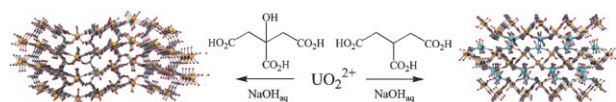


Effective chiral recognition among ions in polar media

Sheba D. Bergman, Richard Frantz, Dalia Gut, Moshe Kol* and Jérôme Lacour*

Effective homochiral recognition occurs between the cationic $[\text{Fe}(\text{eilatin})_3]^{2+}$ complex and TRISPHAT anions even in polar media such as 90% acetone- CHCl_3 (de $\geq 89\%$).

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Uranyl ion complexation by citric and tricarballylic acids: hydrothermal synthesis and structure of two- and three-dimensional uranium-organic frameworks

Pierre Thuéry*

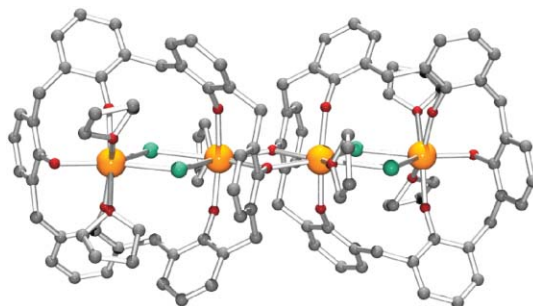
These crystal structures of uranyl citrate and uranyl sodium tricarballylate are the first solid state structural contributions to the old problem of the uranyl-citrate interaction, much investigated for its environmental relevance.

856

Uranium(IV) complexes of calix[*n*]arenes (*n* = 4, 6 and 8)

Lionel Salmon,* Pierre Thuéry and Michel Ephritikhine*

Reaction of UCl_4 with calix[*n*]arenes (*n* = 4, 6 and 8) in THF or pyridine gave the mononuclear $[\text{UCl}_2(\text{calix}[4]\text{arene} - 2\text{H})(\text{THF})_2]$, bis-binuclear $[\text{U}_2\text{Cl}_2(\text{calix}[6]\text{arene} - 6\text{H})(\text{THF})_3]_2$ and trinuclear $[\text{Hpy}]_6[\text{U}_3\text{Cl}_{11}(\text{calix}[8]\text{arene} - 7\text{H})]$ complexes, respectively, which are the first U^{IV} complexes of O-unsubstituted calixarenes.

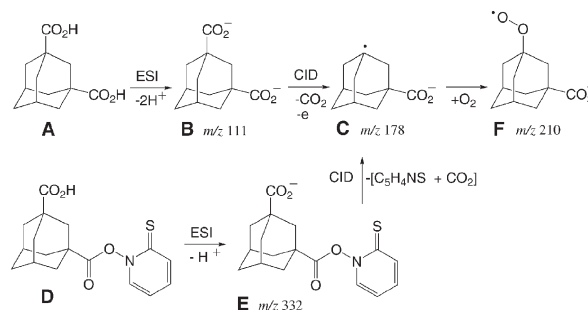


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Trapping of a *tert*-adamantyl peroxy radical in the gas phase

David G. Harman and Stephen J. Blanksby*

A bridgehead adamantyl peroxy radical has been prepared and isolated in the gas phase by the reaction of a distonic radical anion with dioxygen in a quadrupole ion-trap mass spectrometer.

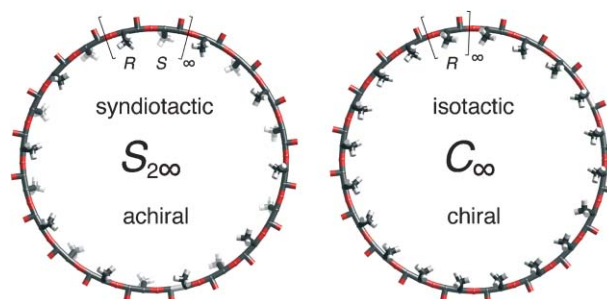


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Application of the $S_{2\infty}$ and C_∞ point groups for the prediction of polymer chirality

Stephen A. Miller*

Polymer chirality assignment is achieved with the first chemical applications of the $S_{2\infty}$ and C_∞ molecular point groups to infinite cyclic polymers, obviating the usual dependence on translational symmetry operations.

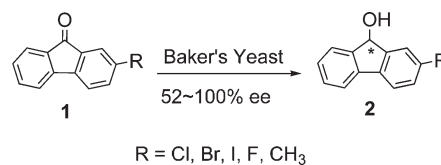


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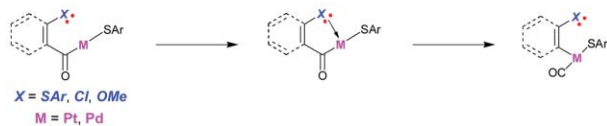
Baker's yeast-mediated enantioselective reduction of substituted fluorenones

Feng Li, Jingnan Cui,* Xuhong Qian,* Weimin Ren and Xingyong Wang

In the presence of DMSO as co-solvent and under vigorous agitation, baker's yeast in water was found to reduce substituted fluorenones to the corresponding fluorenols in good to excellent enantioselectivities.



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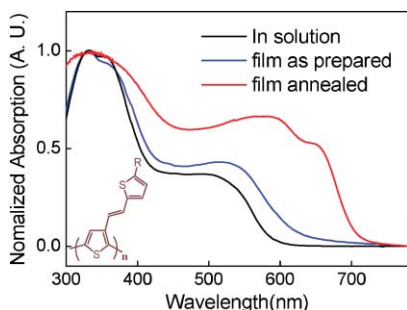


“ β -*cis*-SAr effect” on decarbonylation from α,β -unsaturated acyl and aroyl complexes

Tomohiro Kato, Hitoshi Kuniyasu,* Takamichi Kajjura, Yasunori Minami, Atsushi Ohtaka, Masanori Kinomoto, Jun Terao, Hideo Kurosawa and Nobuaki Kambe*

Lone pair of heteroatom located at the β -*cis* position in α,β -unsaturated acyl and aroyl group 10 metal complexes dramatically facilitated the stoichiometric and catalytic decarbonylation reactions.

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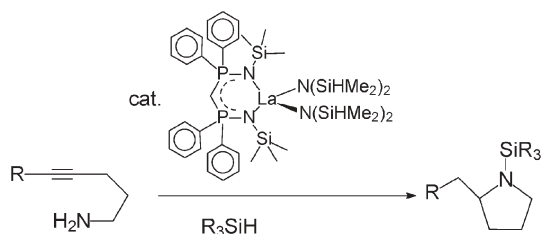


Poly[3-(5-octyl-thienylene-vinyl)-thiophene]: A side-chain conjugated polymer with very broad absorption band

Jianhui Hou, Chunhe Yang, Chang He and Yongfang Li*

A novel polythiophene derivative, poly[3-(5-octyl-thienylene-vinyl)-thiophene] (POTVT) with conjugated thienylene vinyl side-chain, was synthesized. The POTVT film shows a broad absorption covering 300 ~ 700 nm after thermal annealing at 130 °C.

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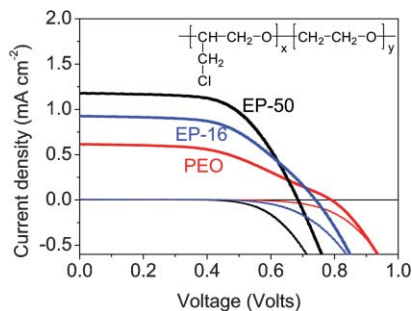


A bis(phosphinimino)methanide lanthanum amide as catalyst for the hydroamination/cyclisation, hydrosilylation and sequential hydroamination/hydrosilylation catalysis

Marcus Rastätter, Agustino Zulys and Peter W. Roesky*

[La{N(SiHMe₂)₂}₂{CH(PPh₂NSiMe₃)₂}] was used as catalyst for the hydroamination/cyclisation, the hydrosilylation and a sequential hydroamination/hydrosilylation reaction.

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Kinetic competition in flexible dye sensitised solar cells employing a series of polymer electrolytes

Hari M. Upadhyaya, Narukuni Hirata, Saif A. Haque, Marco-A de Paoli and James R. Durrant*

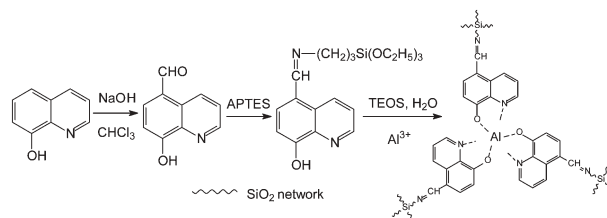
Transient absorption spectroscopy is employed to study electron transfer dynamics in dye sensitised solar cells employing a series of polymer electrolytes, and correlated with device current–voltage characteristics.

880

A covalently bonded AlQ₃/SiO₂ hybrid material with blue light emission by a conventional sol-gel approach

Hongyu Zeng, Weimin Huang and Jianlin Shi*

We report the first example of covalently bonded AlQ₃/silica hybrid materials by a conventional sol-gel approach. The hybrid material is highly solution-processable and shows significant blue light emission and good chemical stability.

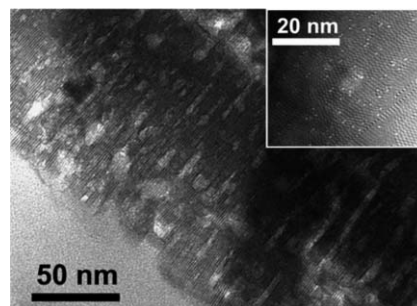


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Generation of hierarchical pore systems in the titanosilicate ETS-10 by hydrogen peroxide treatment under microwave irradiation

Claudiu C. Pavel and Wolfgang Schmidt*

Supermicropores and well-defined mesopores with an average size of 10 nm were created in ETS-10 structure by H₂O₂ treatment under microwave irradiation. Macropores also formed and the external surface area of the material was significantly increased.

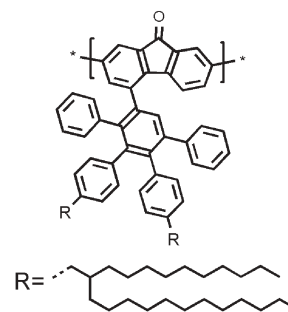


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Synthesis of a soluble poly(flourenone)

Luke Oldridge, Marcel Kastler and Klaus Müllen*

The synthesis and characterisation of a soluble poly(flourenone) is presented, a polymer with high electron affinity with potential for use in plastic electronic devices as an n-type material.

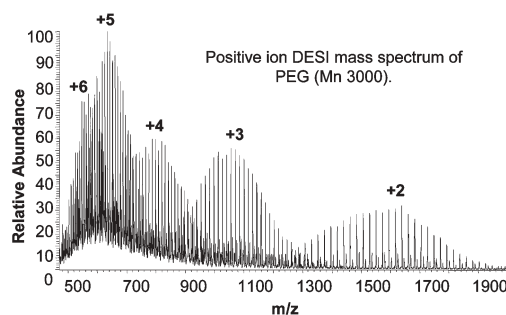


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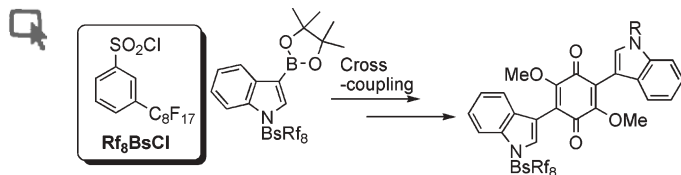
Desorption electrospray ionization and electrosonic spray ionization for solid- and solution-phase analysis of industrial polymers

Marcela Nefliu, Andre Venter and R. Graham Cooks*

Desorption electrospray ionization (DESI) and electrosonic spray ionization (ESSI), two new techniques, are used to measure average molecular weights and molecular weight distributions of solid-phase and solution-phase samples of the same polymers.



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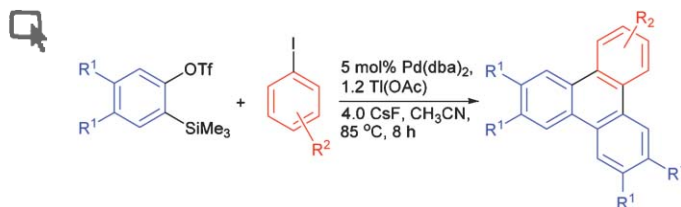


Fluorous-tagged indolylboron for the diversity-oriented synthesis of biologically-attractive bisindole derivatives

Takahiro Kasahara and Yoshinori Kondo*

Sulfonyl type fluorous-tagged indolylboron was used for the high throughput synthesis of a biologically-attractive indole library by palladium catalyzed cross-coupling.

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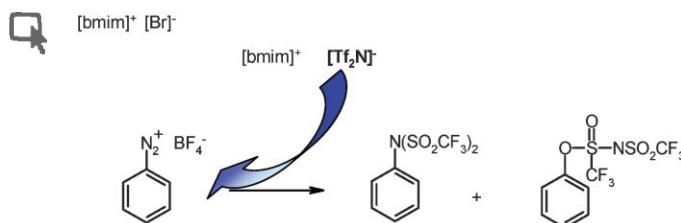


Palladium-catalyzed carbopalladation and carbocyclization of arynes with aryl halides: a highly efficient route to functionalized triphenylenes

Thiruvellore Thatai Jayanth and Chien-Hong Cheng*

Highly substituted triphenylene derivatives were prepared in good yields *via* the palladium-catalyzed carbocyclization of arynes with aryl iodides.

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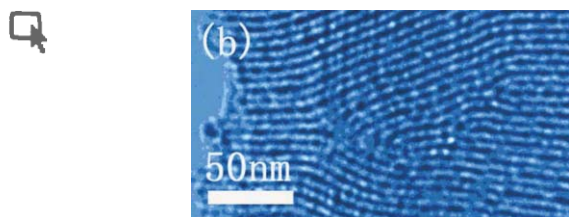


The “non-nucleophilic” anion [Tf₂N][−] competes with the nucleophilic Br[−]: an unexpected trapping in the diazotiation reaction in ionic liquids

Riccardo Bini, Cinzia Chiappe,* Elisa Marmugi and Daniela Pieraccini

Imidazolium ionic liquids containing [Tf₂N][−] are not as innocent as they are often considered. [Tf₂N][−] anion is more reactive than Br[−] in heterolytic diazotiation reactions. This behaviour has been interpreted considering the different association of the two anions with [bvim]⁺ cation inside the IL network.

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Mesoporous silicon oxynitride thin films

Jiacheng Wang and Qian Liu*

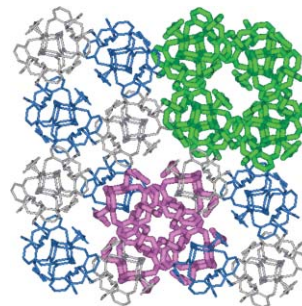
Highly-ordered, pore-modified with amine groups, and glasslike mesoporous silicon oxynitride thin films were prepared by heat treatment of as-synthesized mesoporous silica thin films in a flowing ammonia environment at high temperatures.

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Assembly of a novel supramolecular synthon of calix[4]arene presenting four carboxylic acids

Adina Lazar, Oksana Danylyuk, Kinga Suwinska, Florent Perret and Anthony W. Coleman*

The structure of calix[4]arene tetrabutyroxy-carboxylic acid reveals highly complex packing with pores, helices and interlocking grids, all based on simple carboxylic acid dimers.

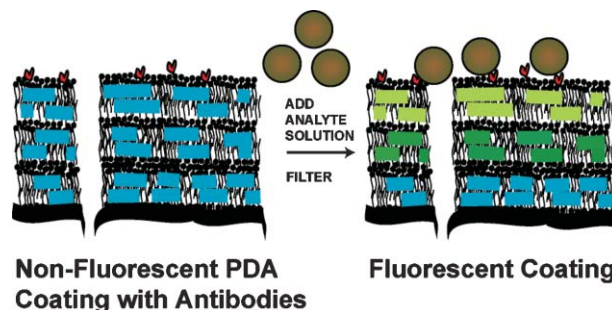


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Antibody-functionalized polydiacetylene coatings on nanoporous membranes for microorganism detection

Bradford A. Pindzola, Anh Tram Nguyen and Mary A. Reppy*

The preparation and characterization of coatings made from polydiacetylene colloids on nano- and microporous membranes and their potential for the detection of microorganisms are presented.

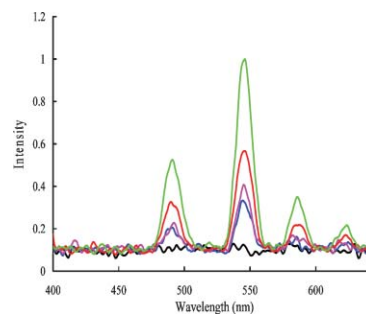


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A luminescent probe containing a tuftsin targeting vector coupled to a terbium complex

Rebecca J. Aarons, Jatinder K. Notta, Marco M. Meloni, Jianghua Feng, Rishma Vidyasagar, Johanna Narvainen, Stuart Allan, Neil Spencer, Risto A. Kauppinen, John S. Snaith* and Stephen Faulkner*

Orthogonal protection strategies have been used to prepare a series of luminescent and MRI active lanthanide complexes containing a tuftsin targeting vector that are internalised by macrophage cells.

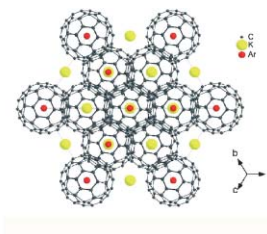
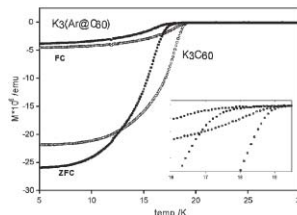


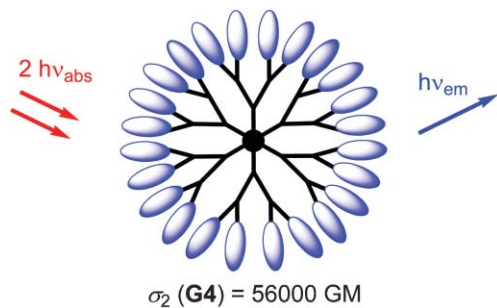
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Superconductivity of doped Ar@C₆₀

A. Takeda, Y. Yokoyama, S. Ito, T. Miyazaki, H. Shimotani, K. Yakigaya, T. Kakiuchi, H. Sawa, H. Takagi, K. Kitazawa and N. Dragoie*

Doped argon endohedral fullerenes show a decrease in the superconductivity critical temperature.





A modular approach to two-photon absorbing organic nanodots: brilliant dendrimers as an alternative to semiconductor quantum dots?

Olivier Mongin, Thatavarathy Rama Krishna, Martinus H. V. Werts, Anne-Marie Caminade, Jean-Pierre Majoral* and Mireille Blanchard-Desce*

Nanoscale fluorescent dendrimers having up to 96 two-photon chromophores and showing very large two-photon absorption cross-sections (up to 56 000 GM) were designed as a complementary “organic” alternative to quantum dots.



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