

IN THIS ISSUE

ISSN 1144-0546 CODEN NJCHES 31(6) 773-1024 (2007)



Cover

See Fabrizio Mancin and Paolo Tecilla, p. 800. Small Pac-zincs are "eating" DNA, illustrating the potency of zinc(II) complexes as catalysts for the hydrolytic cleavage of phosphate diester bonds. Image reproduced by permission of Fabrizio Mancin and Paolo Tecilla from *New. J. Chem.*, 2007, **31**, 800.



Inside Cover

See Masayuki Takeuchi and Seiji Shinkai *et al.*, p. 790. Textile-like well-organized assemblies are obtained by nanoscale alignment of conjugated polymers by a supramolecular approach (the central Chinese character means textile). Image reproduced by permission of Rie Wakabayashi, Kenji Kaneko, Masayuki Takeuchi and Seiji Shinkai from *New. J. Chem.*, 2007, **31**, 790.

CHEMICAL SCIENCE

C41

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

Chemical Science

June 2007/Volume 4/Issue 6

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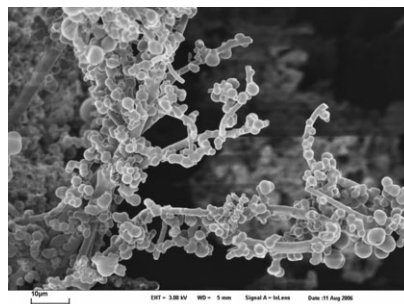
OPINION

787

Back in the black: hydrothermal carbonization of plant material as an efficient chemical process to treat the CO₂ problem?

Maria-Magdalena Titirici, Arne Thomas and Markus Antonietti*

A chemical process, hydrothermal carbonization (HTC) of low value biomass, is discussed as a tool for the sequestration of atmospheric CO₂. The picture shows carbonaceous microparticles made from sugar-beet waste.



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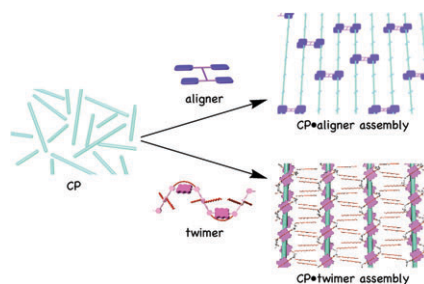
PERSPECTIVES

790

Toward the alignment of conjugated polymers into anisotropically-ordered structure

Rie Wakabayashi, Kenji Kaneko, Masayuki Takeuchi* and Seiji Shinkai*

For the segregation of polymers in individual chains and the controlled alignment of conjugated polymers, we here introduce two different approaches where one is to utilize a crosslinking molecule ('aligner') and the other is to use a twining polymer ('twimer') for organizing conjugated polymers.

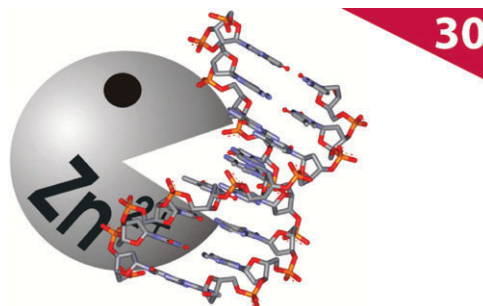


800

Zinc(II) complexes as hydrolytic catalysts of phosphate diester cleavage: from model substrates to nucleic acids

Fabrizio Mancin and Paolo Tecilla

30th Anniversary article: Recent advances and future perspectives in the realization of Zn^{2+} based phosphate diester hydrolytic agents are examined in this Perspective.

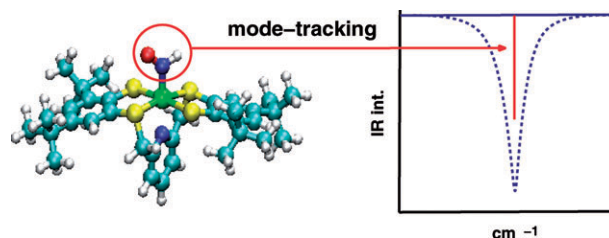


818

Finding a needle in a haystack: direct determination of vibrational signatures in complex systems

Carmen Herrmann, Johannes Neugebauer and Markus Reiher*

The mode-tracking algorithm for *selectively* calculating molecular vibrational frequencies and normal modes is reviewed, which works by diagonalization of the Hessian *via* subspace iteration using a pre-defined initial guess for the normal mode(s) of interest.



LETTERS

832

Estimation of the van der Waals radii of the d-block elements using the concept of bond valence

Samik Nag, Kamalika Banerjee and Dipankar Datta*

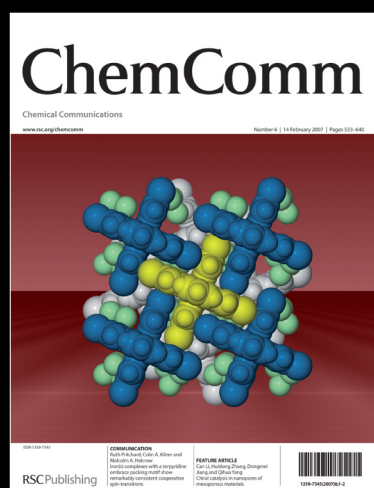
This equation, devised from the concept of bond valence, is used to estimate the van der Waals radius (R) of a d block element M with prior knowledge of the R_X of a non-metal X and r_0 , the bond valence parameter characteristic of the $M-X$ bond.

$$R_M = r_0 + 1.704 - R_X$$

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LETTERS

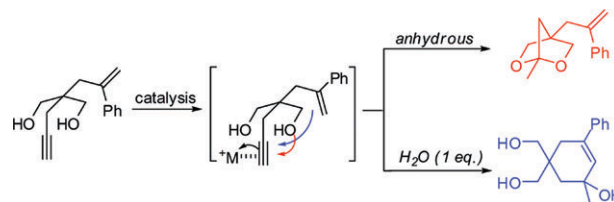


835

Silver-catalyzed intramolecular oxycyclization of alkynes to bridged bicyclic ketals

Chang Ho Oh,* Hyun Jik Yi and Ji Ho Lee

We have discovered a new and highly convenient Ag-catalyzed intramolecular oxycyclization of alkynes, leading to bridged bicyclic ketals as four carbon synthetic building blocks.

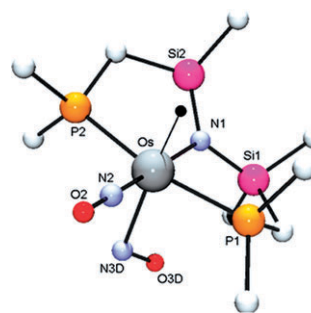


838

Reactivity of $\cdot\text{NO}$ with an osmium polyhydride: Reductive elimination and reductive nitrosylation on the path from odd- to even-electron molecules

Joo-Ho Lee, Hongjun Fan, Maren Pink and Kenneth G. Caulton*

The reaction of radical $\cdot\text{NO}$ with even-electron $(\text{PNP})\text{Os}(\text{H})_3$ occurs by the interplay of one- and two-electron pathways.



PAPERS

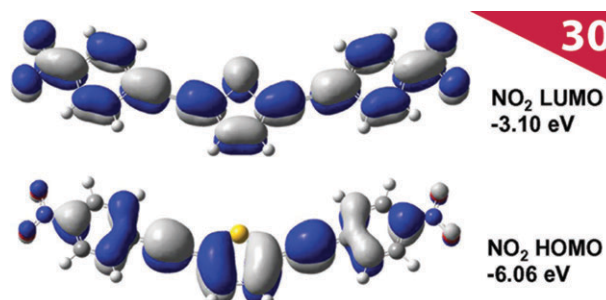


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Synthesis, photophysics and molecular structures of luminescent 2,5-bis(phenylethynyl)thiophenes (BPETs)

Jamie S. Siddle, Richard M. Ward, Jonathan C. Collings, Simon R. Rutter, Laurent Porrès, Lucas Applegarth, Andrew Beeby, Andrei S. Batsanov, Amber L. Thompson, Judith A. K. Howard, Abdou Boucekkine, Karine Costuas, Jean-François Halet and Todd B. Marder*

30th Anniversary article: Strong donors or acceptors ($4\text{-D/A-C}_6\text{H}_4\text{-}$) red-shift absorption and emission bands of 2,5-BPETs, which have moderate quantum yields and short singlet lifetimes characteristic of rapid ISC.



852

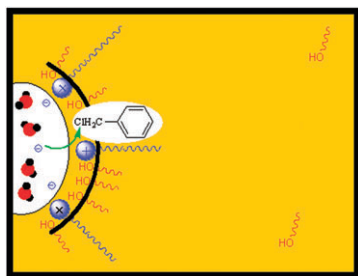
A new class of “all-metal” aromatic hydrido-bridged binary coinage metal heterocycles. A DFT study

Athanassios C. Tsipis* and Alexandros V. Stalikas

A comprehensive study of the structural, energetic, spectroscopic and electronic properties of these metal heterocycles characterized by a common ring-shaped electron density is presented.



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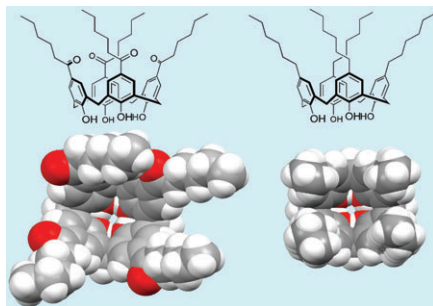
Application of the pseudophase ion-exchange model to reactivity in quaternary water in oil microemulsions

Luis García-Río and Pablo Hervella

The influence of the cosurfactant varying the volume of the interface and the ionic exchange of the reactive ionic nucleophiles is considered to explain reactivity in quaternary water in oil microemulsions.



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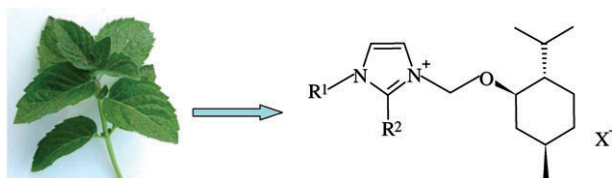
α -C=O provides access to the cavity in acyl calix[4]arenes: A comparative study of crystal structures

Michaela Pojarova, Gennady S. Ananchenko,* Konstantin A. Udachin, Florent Perret, Anthony W. Coleman and John A. Ripmeester

The accessibility of the cavity in calix[4]arenes strongly depends on the length of the *para*-substituent and its ability to conjugate with phenyl groups.



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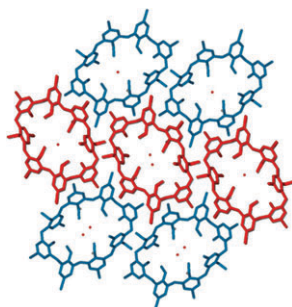
Synthesis and properties of chiral imidazolium ionic liquids with a (1*R*,2*S*,5*R*)-(–)-menthoxymethyl substituent

Juliusz Pernak,* Joanna Feder-Kubis, Anna Cieniecka-Rosłonkiewicz, Cedric Fischmeister, Scott T. Griffin and Robin D. Rogers*

Hydrophilic and hydrophobic chiral imidazolium ionic liquids in which the chirality originates from the cation have been synthesized and characterized.



893



Synthesis, solid state structures and interfacial properties of new *para*-phosphonato-*O*-alkoxy-calix[8]arene derivatives

Florent Perret, Kinga Suwinska, Bernard Bertino Ghera, Hélène Parrot-Lopez and Anthony W. Coleman*

The synthesis of six *para*-phosphonato-alkoxy-calix[8]arene derivatives are described. The interfacial properties of the *para*-phosphonato-alkoxy-calix[8]arene derivatives and their di-*iso*-propoxy-protected analogues have been determined.

PAPERS



901

Steered molecular dynamics studies reveal different unfolding pathways of prions from mammalian and non-mammalian species

Matteo Pappalardo, Danilo Milardi, Domenico Grasso and Carmelo La Rosa*

Steered molecular dynamics have been employed to assess the unfolding resistance to external forces of mammalian and non-mammalian prions. Prions from mammalian species exhibited a twofold resistance to mechanical unfolding when compared to their non-mammalian counterparts.

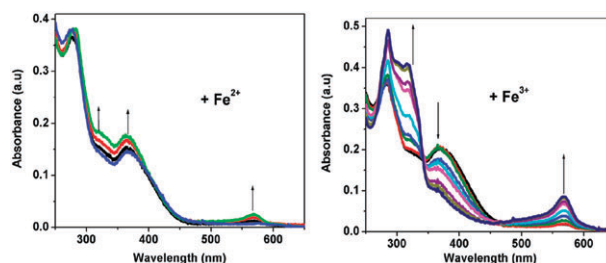


906

A highly selective colorimetric chemosensor for detecting the respective amounts of iron(II) and iron(III) ions in water

Zuo-Qin Liang, Cai-Xia Wang, Jia-Xiang Yang,* Hong-Wen Gao, Yu-Peng Tian, Xu-Tang Tao and Min-Hua Jiang

A colorimetric chemosensor for iron has been synthesized and it can detect the respective amounts of Fe(II) and Fe(III).

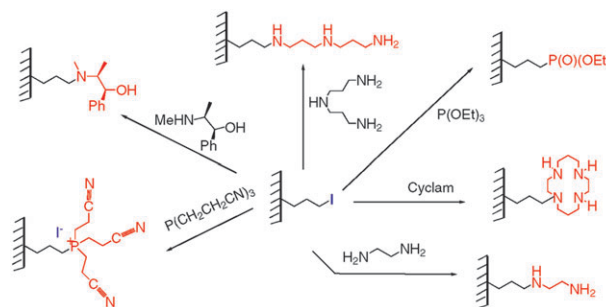


911

Direct synthesis of ordered mesoporous silica containing iodopropyl groups. A useful function for chemical modifications

Johan Alauzun, Ahmad Mehdi,* Catherine Reyé and Robert Corriu*

The templated synthesis of iodopropyl-functionalized mesostructured silica was achieved by the co-condensation of iodopropyltriethoxysilane and tetraethylorthosilicate in presence of hydrogen iodide as an acid catalyst. Their easy chemical modification was clearly evidenced.

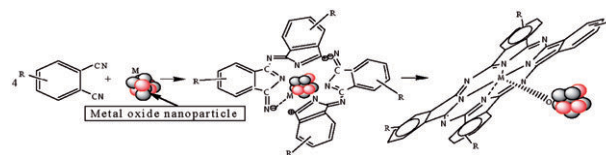


916

In situ chemical formation of iron phthalocyanine (FePc) monolayer on the surface of magnetite nanoparticles

Shiyong Liu, Xuanzhen Jiang* and Guanglan Zhuo

The under-coordinated Fe sites on the surface of SCFD-derived Fe₃O₄ nanoparticles and phthalic nitrile act as template ions and components, respectively, for the formation of FePc monolayer-coated Fe₃O₄ NPs.



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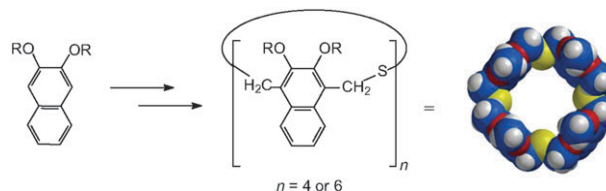
PAPERS

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Synthesis and complexation study of (1,4-linked)-homothiaisocalixnaphthalenes

Huu-Anh Tran and Paris E. Georghiou*

The synthesis and some properties of the targeted (1,4-linked)-homothiaisocalixnaphthalenes is described.

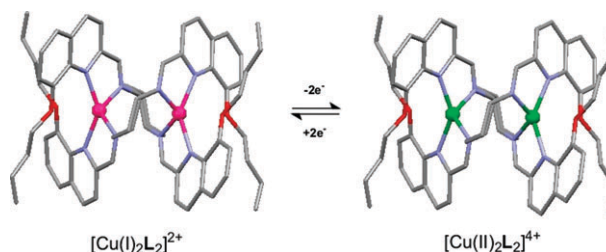


927

Enhanced kinetic inertness in the electrochemical interconversion of Cu(I) double helical to Cu(II) monomeric complexes

Piersandro Pallavicini,* Massimo Boiocchi, Giacomo Dacarro and Carlo Mangano

Cu(I) helicates can be reversibly oxidized to Cu(II) helicates that display enhanced kinetic inertness with respect to disassembling.

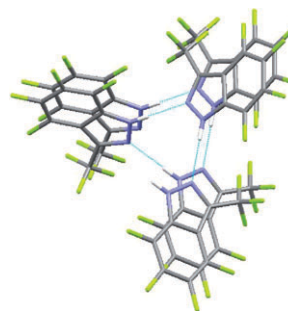


936

The structure of fluorinated indazoles: the effect of the replacement of a H by a F atom on the supramolecular structure of NH-indazoles

Johannes Teichert, Pascal Oulié, Kane Jacob, Laure Vendier, Michel Etienne,* Rosa M. Claramunt,* Concepción López, Carlos Pérez Medina, Ibon Alkorta and José Elguero

An unprecedented family of polyfluorinated indazoles crystallizes in the form of chiral helical catemers.

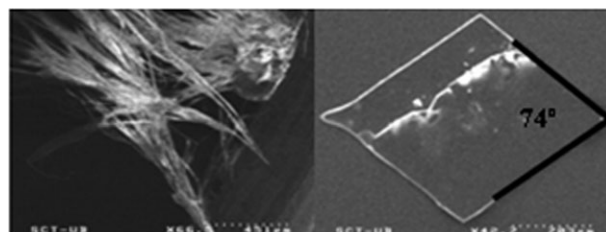


947

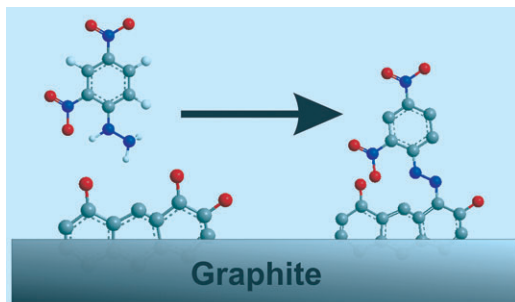
Polymorphism of even saturated carboxylic acids from *n*-decanoic to *n*-eicosanoic acid

Evelyn Moreno, Raquel Cordobilla, Teresa Calvet,* M. A. Cuevas-Diarte, Gabin Gbabode, Philippe Negrier, Denise Mondieig and Harry A. J. Oonk

Seven different forms, including polymorphs and polytypes, are identified and fully characterized for *n*-saturated carboxylic acids.



958

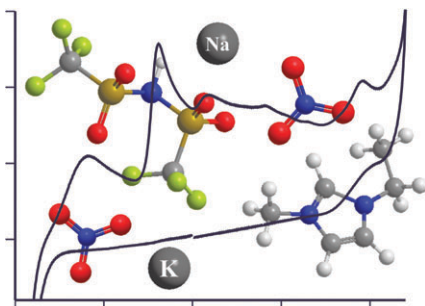


Identifying quinone-like species on the surface of graphitic carbon and multi-walled carbon nanotubes using reactions with 2,4-dinitrophenylhydrazine to provide a voltammetric fingerprint

Charles A. Thorogood, Gregory G. Wildgoose, John H. Jones and Richard G. Compton*

Quinone groups on the surface of graphite and CNTs are labelled both voltammetrically and by XPS using 2,4-dinitrophenylhydrazine.

966

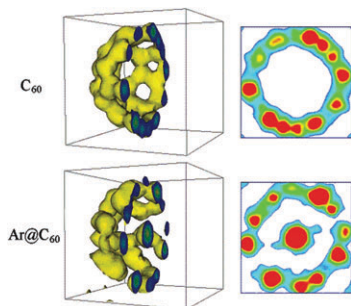


The electrochemical oxidation and reduction of nitrate ions in the room temperature ionic liquid [C₂mim][NTf₂]; the latter behaves as a 'melt' rather than an 'organic solvent'

Tessa L. Broder, Debbie S. Silvester, Leigh Aldous, Christopher Hardacre, Alison Crossley and Richard G. Compton*

Fascinating nitrate 'melt'-like behaviour observed at ambient temperatures in ionic liquids.

973



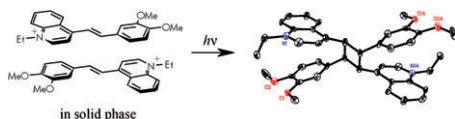
Superconductivity of doped Ar@C₆₀

Kenichi Yakigaya, Atsuhiko Takeda, Yasunori Yokoyama, Seitaro Ito, Takashi Miyazaki, Tomohiro Suetsuna, Hidekazu Shimotani, Toru Kakiuchi, Hiroshi Sawa, Hidenori Takagi, Koichi Kitazawa and Nita Dragoe*

Doped argon endohedral fullerenes showed an unexpected decrease in the superconductivity critical temperature.



980



4-Styrylquinolines: synthesis and study of [2 + 2]-photocycloaddition reactions in thin films and single crystals

Lyudmila G. Kuz'mina,* Artem I. Vedernikov, Natalia A. Lobova, Andrei V. Churakov, Judith A. K. Howard, Michael V. Alfimov and Sergey P. Gromov*

Quinolyphenylethylenes that exhibit in their crystals the head-to-tail packing motif undergo [2 + 2]-photocycloaddition in thin films and single crystals without their degradation.

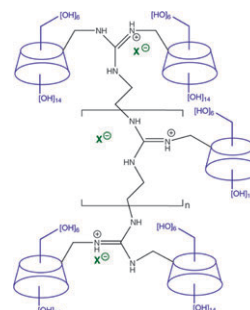
PAPERS

995

Molecular recognition of nucleotides by a new bis(guanidinium)tetrakis(β -cyclodextrin) tetrapod

Stephane Menuel, Raphaël E. Duval, Diana Cuc, Pierre Mutzenhardt and Alain Marsura*

A novel bis(guanidinium)tetrakis(β -cyclodextrin) ($n = 0$) foldamer, designed for gene delivery, its multistep synthesis using the phosphine imide strategy and its formation of bimolecular complexes in water with ATP, ADP and AMP nucleotides are described.

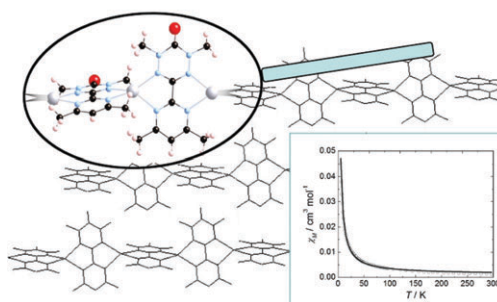


1001

Verdazyl-based extended structures: synthesis, structures and magnetic properties of silver(I) one dimensional compounds

Fabrice Pointillart, Cyrille Train,* Patrick Herson, Jérôme Marrot and Michel Verdaguer*

Verdazyl-based radicals bind to silver(I) ions to form extended one dimensional structures.

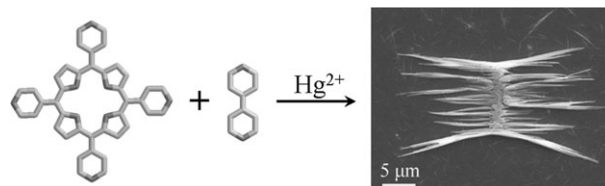


1007

Coordination polymer nanocombs self-assembled at the water–chloroform interface

Bing Liu, Meng Chen, Chikashi Nakamura, Jun Miyake and Dong-Jin Qian*

We report the HgCl_2 -mediated interfacial self-assembly of coordination polymer nanocombs composed of (zinc, palladium) tetrapyrrolylporphyrin and 4,4'-bipyridyl ligands.



1013

Synthesis and zinc(II) complexation modulated fluorescence emission properties of two pyrene-oligo(phenylene vinylene)-2,2'-bipyridine conjugated molecular rods

Stéphanie Leroy-Lhez,* Magali Allain, Jean Oberlé and Frédéric Fages*

A series of conjugated rods in which the pyrene chromophore is connected to a 2,2'-bipyridine unit *via* an oligo(phenylene vinylene) bridge have been synthesized and their photophysical properties in solution investigated.



ADDITIONS AND CORRECTIONS

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Synthesis and properties of chiral imidazolium ionic liquids with a (1*R*,2*S*,5*R*)-(–)-menthoxyethyl substituent

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