



Cover (far left)

Formation of a trimer of carceplexes from a hexamer of cavitands.

Inside cover (left) The supramolecular square structure of the mercury (n) chloride complex of [tetrakis(2-pyrimidinylethynyl) cyclobutadiene][(cyclopentadienyl)cobalt].

contents



Towards artificial muscles at the nanometric level

Maria Consuelo Jimenez-Molero, Christiane Dietrich-Buchecker and



Molecular systems suited to the fabrication of machines and (rotary or linear) motors at the molecular level are outlined, and their possible applications discussed.

extended situation

contracted situation

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EATURE ARTICLE

Molecules that can't resist templation

John Sherman

The encapsulation of molecules or ions has captured the interest of a variety of researches, including those using zeolites, fullerenes, micelles, clathrates, and metal coordination complexes. Multiple hemispherical units have been used to create organic cages that can bind guests reversibly or irreversibly. Often such cages will only form in the presence of a guest, which acts as a template. This article summarizes some of the work in this field.

Grafted conjugated polymers: synthesis and characterization of a polyester side chain substituted poly(*para*phenyleneethynylene)



COMMUNICATIONS



Yqing Wang, Belma Erdogan, James N. Wilson and Uwe H. F. Bunz*

Reported in the synthesis of a poly(*para*phenyleneethynylene) with macromolecular side chains and its irreversible thermochromic behaviour.

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Chemical Communications

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A biosensing model system: selective interaction of biotinylated PPEs with streptavidin-coated polystyrene microspheres

James N. Wilson, Yiqing Wang, John J. Lavigne and Uwe H. F. Bunz*

Formation of a highly fluorescent composite formed from the biotinylated PPE 3 and streptavidin covered polystyrene microspheres is reported.

A supramolecular organometallic-metalorganic square

Matthew Laskoski, Jason G. M. Morton, Mark D. Smith and Uwe H. F. Bunz*

The crystal structure of this highly functionalized cyclobutadiene complex shows the incorporation of mercury chloride in a *trans*-spanning fashion. The mercury chloride shows an unusual square planar coordination geometry.

The first 'two-over/two-under' (2O/2U) 2D weave structure assembled from Hg-containing 1D coordination polymer chains

Yun-Hui Li, Cheng-Yong Su, Andrea M. Goforth, Ken D. Shimizu, Kenneth D. Gray, Mark D. Smith and Hans-Conrad zur Loye*

1D coordination polymers interweave in a 'two-over-two-under' fashion resulting in a 2D cloth-like network. Its formation is made possible by the distorted tetrahedral coordination geometry of the Hg(II) ion and the 'Z' type conformation of the ligand.

Excess electron transfer in flavin-capped, thymine dimer-containing DNA hairpins

Christoph Behrens and Thomas Carell*

Excess electrons hop through DNA using A–T base pairs as temporary charge carriers. This was investigated with flavin-capped and thymine dimer containing DNA hairpins.



Donor-substituted peralkynylated "radiaannulenes": novel all-carbon macrocycles with an intense intramolecular charge-transfer

Frieder Mitzel, Corinne Boudon, Jean-Paul Gisselbrecht, Paul Seiler, Maurice Gross and François Diederich*

Acetylenic scaffolding based on tetraethynylethene (TEE) has been advanced to a novel unusual series of cyclic TEE-oligomers and to unprecedented bicyclic all-carbon sheets. These highly conjugated systems are good electron acceptors and display intense intramolecular charge-transfer when equipped with peripheral electron-donors.





Crystal polymorphism in 1-butyl-3-methylimidazolium halides: supporting ionic liquid formation by inhibition of crystallization

John D. Holbrey, W. Matthew Reichert, Mark Nieuwenhuyzen, Suzanne Johnston, Kenneth R. Seddon and Robin D. Rogers

Crystallization of 1-butyl-3-methylimidazolium chloride from mixed ionic liquid or ionic liquid–aromatic solution, and from the melt yields different crystalline polymorphs, the first direct evidence for inhibition of crystallization in ionic liquids by polymorphism.





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Heck arylation of cyclic enol ethers with aryldiazonium salts: regio- and stereoselective synthesis of arylated oxacycles

Bernd Schmidt

The first examples of the arylation of cyclic enol ethers with aryldiazonium tetrafluoroborates are reported. The reaction is highly *trans*-diastereoselective and undesired double bond isomerization reactions are not observed.

Primary charge separation in photoinduced multielectron storage systems. A dinuclear ruthenium(II) species featuring a charge-separated state with a lifetime of 1.3 µs

Claudio Chiorboli, Sandro Fracasso, Franco Scandola, Sebastiano Campagna, Scolastica Serroni, Rama Konduri and Frederick M. MacDonnell

In the Ru(II) species shown, the initially formed MLCT state is deactivated in 35 ps by electron transfer (cs) to a charge-separated state whose lifetime is extremely solvent dependent, reaching 1.3 μ s in dichloromethane at room temperature.

A novel coordination geometry for the uranyl ion. Rhombohedral uranium environment in $[UO_2(OTf)_2(bpy)_2]$ and $[UO_2(phen)_3][OTf]_2$

Jean-Claude Berthet,* Martine Nierlich and Michel Ephritikhine

In contrast to what has been invariably observed and is considered as a general rule, the UO_2^{2+} ion can adopt a coordination geometry other than the ubiquitous polygonal bipyramid.

The use of a germene for the synthesis of esters of α -germylsubstituted α -amino acid and α -aminophosphonic acid

S. Ech-Cherif El Kettani, J. Escudié, C. Couret, H. Ranaivonjatovo, M. Lazraq, M. Soufiaoui, H. Gornitzka and G. Cretiu Nemes

The first α -germyl-substituted α -amino (or α -aminophosphonic) esters have been synthesized by a one-pot reaction between the germene Mes₂Ge=CR₂ (CR₂ = fluorenylidene) and the iminoester or iminophosphonate Ph(H)C=NCH₂-Y.

A bis-salicylaldiminato Schiff base and its zinc complex as new highly fluorescent red dopants for high performance organic electroluminescence devices

Pengfei Wang, Ziruo Hong, Zhiyuan Xie, Shiwen Tong, Oiyan Wong, Chun-Sing Lee, Ningbew Wong, Liangsun Hung and Shuittong Lee*



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Bright saturated red-emitting EL devices with excellent colour chromaticity coordinates (x, y = 0.670, 0.325 for **BDPMB**; x, y = 0.655, 0.325 for **BDPMB-Zn**) and good efficiency (1.35 cd A⁻¹ for **BDPMB**; 0.50 cd A⁻¹ for **BDPMB-Zn**) were obtained by using **BDPMB** and **BDPMB-Zn** as the novel red-emitting dopants.

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Formation of a palladium(II) complex of 2-(2-pyridinylmethyleneamino)-2'-hydroxy-1,1'-binaphthyl with novel C_σ -coordination and its theoretical investigation

Lijin Xu, Qian Shi, Xingshu Li,* Xian Jia, Xin Huang, Ruihu Wang, Zhongyuan Zhou, Zhenyang Lin* and Albert S. C. Chan*

Complexation of the NOBIN-derived Schiff ligand 1 with $Pd(CH_3CN)_2Cl_2$ has been observed to result in a novel Pd–C bonding mode and theoretical calculations have been carried out to clarify the reaction mechanism.

A highly regio- and stereoselective transition metal-catalyzed hydrosilylation of terminal alkynes under ambient conditions of air, water, and room temperature

Wei Wu and Chao-Jun Li*



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Hydrosilylation of terminal alkynes catalyzed by Pt(DVDS)–P proceeded with high efficiency and stereoselectivity at room temperature in air and water.

An *N*-heterocyclic carbene as a bidentate hemilabile ligand: a synchrotron X-ray diffraction and density functional theory study



Vladimir K. Dioumaev, David J. Szalda, Jonathan Hanson, James A. Franz and R. Morris Bullock*

In CpM(CO)₂(IMes)⁺B(C₆F₅)₄⁻ (M = Mo, W; IMes = 1,3bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) the *N*-heterocyclic carbene ligand IMes adopts a bidentate hemilabile coordination mode, with a C=C bond of one of the mesityl rings of IMes weakly coordinated to the formally 16e⁻ metal center.

Specificity of metal ion cross-linking in marine mussel adhesives

Jennifer Monahan and Jonathan J. Wilker*





Syntheses of second generation, 14-membered ring β-turn mimics

Hong Boon Lee, Mookda Pattarawarapan, Sudipta Roy and Kevin $\mathsf{Burgess}^*$

Practical solid phase syntheses of the peptidomimetics shown have been developed; conformational analyses show their structures present dipeptide fragments in β -turn conformations.

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Anion complexation properties of 2,2'-bisamidodipyrrolylmethanes

Ismael El Drubi Vega, Salvatore Camiolo, Philip A. Gale,* Michael B. Hursthouse and Mark E. Light

New bis-amido dipyrrolylmethanes have been synthesised and shown to complex anions in DMSO/5% solution. The compound shown binds $H_2PO_4^-$ in DMSO- $d_6/25\%$ water with an association constant of 234 M^{-1} .

Synthesis of a novel C2-aryl substituted 1,2-unsaturated pyrrolobenzodiazepine

Gyoung-Dong Kang, Philip W. Howard* and David E. Thurston*



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A novel C2-aryl 1,2-unsaturated PBD has been prepared *via* an enol triflate intermediate. The regiochemistry of triflation is dependent upon the point at which the reaction is performed during the synthetic route.



A dicobalt(II) complex of a triazolate-containing macrocycle reacts with nitromethane to yield an organometallic dicobalt(III) complex

Udo Beckmann, Janna D. Ewing and Sally Brooker*

Two different dinuclear cobalt complexes of a triazolate-containing Schiff-base macrocycle have been prepared. The dinuclear cobalt(II) complex readily reacts with nitromethane in air to form a dinuclear cobalt(III) complex with two Co–C nitromethyl bonds.



Concerted interaction between conjugated double bond CHs and multiple OHs in polyene macrolide antibiotic chainin: weak = $C-H\cdots O$ interactions responsible for intrinsic molecular assembly

Yasuko In, Hirofumi Ohishi, Toshimasa Ishida* and Yasuhiro Igarashi*

The concerted interactions observed between five conjugated double bond CHs and four hydroxy Os in the crystal of chainin, a polyene macrolide antibiotic, clarified the existence of unprecedented, weak = $C-H\cdots O$ interactions, which is important for forming its intrinsic molecular assembly.

Variations in the solid-state, solution and theoretical structures of a laterally deprotonated aromatic tertiary amide



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David R. Armstrong, Jonathan Clayden,* Robert Haigh, David J. Linton, Paul Schooler and Andrew E. H. Wheatley*

The structural chemistry of a laterally deprotonated 2-alkyl-1naphthamide is investigated in the solid state, in solution and by DFT calculations.

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COMMUNICATIONS

Reactions of nitrogen oxides with heme models. Low temperature spectral characterization of the unstable nitrato-nitrosyl complex Fe^{III}(TPP)(ONO₂)(NO)

Tigran S. Kurtikyan,* Garik G. Martirosyan, Manya E. Hakobyan and Peter C. Ford*

Low temperature interaction of NO gas with $Fe(TPP)(O_2NO)$ thin films leads to formation of a new 6-coordinate complex, $Fe(TPP)(ONO_2)(NO)$. The reaction is accompanied by bidentate–monodentate isomerization of coordinated nitrate and transition of Fe(III) from high-spin to low-spin.

Coordination complex between haemin and parallelquadruplexed d(TTAGGG)

Toshiyasu Mikuma, Takako Ohyama, Norifumi Terui, Yasuhiko Yamamoto* and Hiroshi Hori

Haemin, iron(III)–protoporphyrin IX complex, and parallelquadruplexed d(TTAGGG) have been shown to form a stable coordination complex which exhibits spectroscopic properties remarkably similar to those of haemoproteins.

F F O F F

Chemical shift (ppm)

Fluoroperylene diimide: a soluble and air-stable electron acceptor

Min-Min Shi, Hong-Zheng Chen,* Jing-Zhi Sun, Jian Ye and Mang Wang*

Fluorinated perylene diimide (1) possessed particular advantages: good solubility and lower LUMO while compared to its non-fluorinated analog.
Thus, 1 exhibited much better photoconductivity whether charged negatively or positively.

R

Simple preparation of monodisperse hollow silica particles without using templates



Hoe Jin Hah, Jung Soo Kim, Byung Jun Jeon, Sang Man Koo* and Yong Eun Lee

Monodisperse hollow silica particles were prepared *via* a simple two-step method without using templates. The particle size and hollow diameter of the resultant particles can be controlled by changing the experimental conditions.

A novel one-pot three-component tandem

Michael/aldol/Horner–Wadsworth–Emmons (HWE) reaction of lithium alkylselenolates with 1-alkynylphosphine oxides and aldehydes: facile synthesis of selenium-substituted allenes

Xian Huang* and Zheng-Chang Xiong



The one-pot tandem Michael/aldol/Horner–Wadsworth–Emmons (HWE) reaction of lithium alkylselenolates, 1-alkynylphosphine oxides and aldehydes in THF provides a new general access to selenium-substituted allenes with good to excellent yields.



Spontaneous free-standing nanostructured film growth in polyelectrolytesurfactant systems



Karen J. Edler,* Arach Goldar, Tessa Brennan and Stephen J. Roser

Substitution of a polyelectrolyte for silica during formation of surfactant-templated films produces similar nano- and macroscale structures confirming that silica acts as a polyelectrolyte during self-assembly of nanostructured thin films.

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Masilamani Jeganmohan, Muthian Shanmugasundaram and Chien-Hong Cheng*



The three-component assembling reaction of allenes, aryl iodides and stannylgermane catalyzed by the Pd(dba)₂-toluene system affords 2arylallylgermanes in good to excellent yields.

From manganese(II)-azido layers to a novel three-dimensional molecular magnet: spin canting and metamagnetism

En-Qing Gao, Zhe-Ming Wang and Chun-Hua Yan*

Two-dimensional magnetically active Mn^{II}-azido layers are interlinked by an organic spacer to generate a 3D pillared structure. The compound exhibits metamagnetic behavior due to spin canting within the antiferromagnetic layers and interlayer antiferromagnetic interactions.

Synthesis, structure and catalytic activity of an air-stable titanium triflate, supported by an amine tris(phenolate) ligand

Steven D. Bull, Matthew G. Davidson, Andrew L. Johnson, Diane E. J. E. Robinson and Mary F. Mahon

An air- and moisture-stable titanium(IV) triflate (**3**) supported by a C_3 -symmetric amine tris(phenolate) ligand (1a) has been synthesised, characterised by X-ray crystallography and demonstrated to be an excellent catalyst for formal aza-Diels-Alder reactions.

A novel route to the fluorinated diimines: carbon monoxide-promoted reductive homocoupling of fluorinated imidoyl iodides in the presence of a palladium catalyst

Hideki Amii, Mitsuhiro Kohda, Motoharu Seo and Kenji Uneyama*

A new catalytic access to the fluorinated α -dimines which involves palladium(0)catalyzed reductive dimerization of the imidoyl iodides is described.



cat. Pd(0)

со

Bis-functionalized fullerene-dibenzo[18]crown-6 conjugate: synthesis and cation-complexation dependent redox behavior

Phillip M. Smith, Amy Lea McCarty, Nhu Yen Nguyen, Melvin E. Zandler and Francis D'Souza*

A one-step procedure to synthesize a bis-functionalized fullerene-crown ether conjugate by 1,3-dipolar cycloaddition of azomethine ylides to C₆₀ and metal ion induced potential changes of the C60 redox processes as electrochemical evidence for cation recognition is reported.

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Reversible formation of excited states in intramolecular donor assisted chemiluminescence reactions of dioxetanes

Sharat Singh and Edwin F. Ullman*

Equilibrium donor substituted dioxetanes are in thermal equilibrium with excited charge transfer states that undergo concomitant ring scission and energy transfer to energy acceptors to yield excited state products.

Bis(phosphinimino)methyl derivatives of Ca, Sr and Ba: facile access to heavier alkaline earth organometallic chemistry

Michael S. Hill* and Peter B. Hitchcock

A series of mononuclear and arene-soluble bis(phosphinimino)methyl derivatives of the heavier alkaline earth metals, calcium, strontium and barium, have been obtained by straightforward addition of two molar equivalents of $[KN(SiMe_3)_2]$ to a mixture of $[CH_2(Ph_2P=NC_6H_2-Me_3-2,4,6)_2]$ and MI_2 (M = Ca, Sr, Ba) in THF.

[{AuTl(C₆Cl₅)₂(toluene)}₂(dioxane)]: A striking structure that leads to a blue luminescence

Eduardo J. Fernández, Antonio Laguna,* José María López-de-Luzuriaga, M. Elena Olmos and Javier Pérez

The blue luminescent complex [{AuTl(C_6Cl_5)₂(toluene)}₂(dioxane)] displays the shortest Au–Tl interaction, a toluene molecule in a η^6 -mode and the "disappearance" of the Tl(I) inert pair.

3-Chloropropenyl pivaloate in organic synthesis: the first asymmetric catalytic entry to *syn*-alk-1-ene-3,4-diols



Marco Lombardo,* Sebastiano Licciulli, Stefano Morganti and Claudio Trombini*

A new route to enantiomerically enriched *syn*-alk-1-ene-3,4-diols was developed by applying the Salen-based asymmetric version of the chromium-catalysed Nozaki–Hiyama–Kishi protocol to the reaction of 3-chloropropenyl pivaloate with aldehydes.



Active, selective, and stable Pt/Na-[Fe]ZSM5 catalyst for the dehydrogenation of light alkanes

Toshio Waku, Joseph A. Biscardi and Enrique Iglesia*

Small Pt clusters in Na-[Fe]ZSM5 give high alkene selectivities, nearequilibrium alkene yields, and unprecedented stability in the catalytic dehydrogenation of light alkanes.

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Lescop, Loic Toupet, Jean-François Halet and Régis Réau*

Complexes 1 isomerise into their thermodynamically more stable isomers 2 providing a straightforward and stereospecific route to the first P,N-ligands featuring a phospholene unit.

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Enantioselectivity in the catalytic hydroesterification of acenaphthylene: direct evidence of the racemization of Pd^{II} -alkyl species by a degenerate substitution equilibrium with $Pd^{0}L_{n}$

Jordi Gironès, Josep Duran, Alfonso Polo* and Julio Real

enantioselectivity for hydrogenation of an alkyl-aryl ketone

A mono-TTF-annulated porphyrin as a fluorescence switch

A degenerate substitution equilibrium between $Pd^{0}L_{n}$ and the Pd^{II} -alkyl species was observed in the palladium catalyzed hydroesterification of acenaphthylene. This process involves the inversion of the alkyl carbon, producing a detrimental effect in the enantioselectivity of the reaction.

A ruthenium catalyst that does not require an N-H ligand to achieve high

ADDITIONS AND CORRECTIONS

Carolyn G. Leong, Okwado M. Akotsi, Michael J. Ferguson and Steven H. Bergens

Hongchao Li, Jan O. Jeppesen, Eric Levillain and Jan Becher



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David O'Donoghue and Edmond Magner The redox thermodynamics of microperoxidase are dependent on the solvent medium

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