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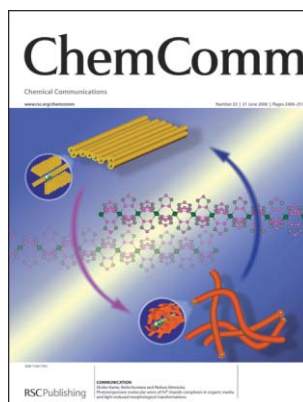
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (23) 2409–2516 (2006)



Cover

See William I. F. David, Paul A. Anderson *et al.*, page 2439. Synthesis and structure of the new complex hydride $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$ solved from synchrotron X-ray and neutron powder diffraction data. Image reproduced by permission of Philip A. Chater, William I. F. David, Simon R. Johnson, Peter P. Edwards and Paul A. Anderson from *Chem. Commun.*, 2006, 2439.



Inside cover

See Nobuo Kimizuka *et al.*, page 2442. Photoresponsive molecular wires of lipophilic Fe(II) 1,2,4-triazole complexes in organic media and their controlled self-assembly. Image reproduced by permission of Shoko Kume, Keita Kuroiwa and Nobuo Kimizuka from *Chem. Commun.*, 2006, 2442.

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 2006/Volume 3/Issue 6

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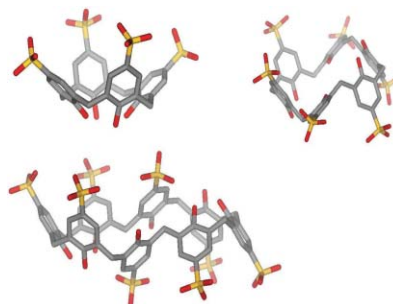
FEATURE ARTICLE

2425

Biochemistry of the *para*-sulfonato-calix[n]arenes

Florent Perret, Adina N. Lazar and Anthony W. Coleman*

The biochemistry of the *para*-sulfonato-calix[n]arenes has shown rapid development during the past ten years, the highly diverse biomedical applications of these molecules now include anti-viral, anti-thrombotic activities, enzyme blocking and protein complexation. The future is even more promising as *para*-sulfonato-calix[n]arenes have, now, been shown to have potential in the diagnosis of prion-based diseases. Their innocuous nature, as far as is known at present, may open up their future use in medications.



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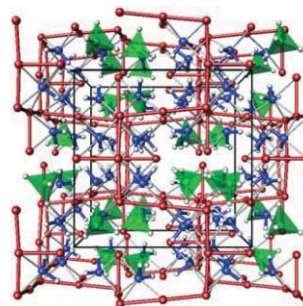
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2439

Synthesis and crystal structure of $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$

Philip A. Chater, William I. F. David,* Simon R. Johnson, Peter P. Edwards and Paul A. Anderson*

The structure of the new complex hydride $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$ formed by the reaction of LiBH_4 with LiNH_2 solved by computational methods from synchrotron X-ray and neutron powder diffraction data.

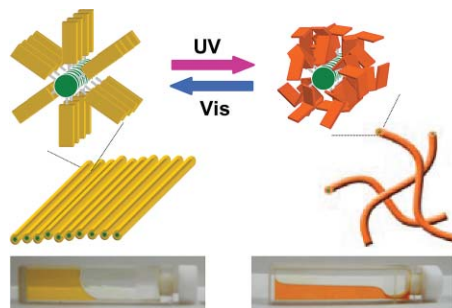


2442

Photoresponsive molecular wires of Fe^{II} triazole complexes in organic media and light-induced morphological transformations

Shoko Kume, Keita Kuroiwa and Nobuo Kimizuka*

Photomanipulation of lipophilic 1D metal complexes leads to reversible control over morphology, assembly and the gel-to-sol transition in organic media.

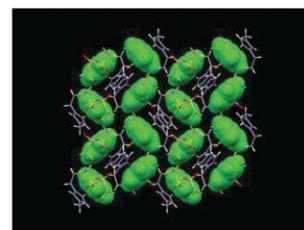
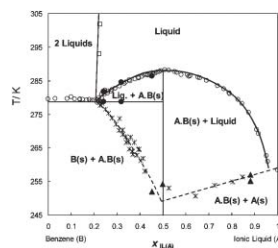


2445

Condensed phase behaviour of ionic liquid–benzene mixtures: congruent melting of a $[\text{mim}][\text{NTf}_2] \cdot \text{C}_6\text{H}_6$ inclusion crystal

Joanna Óachwa, Isabel Bento, M. Teresa Duarte, José N. Canongia Lopes and Luís P. N. Rebelo*

The solid–liquid phase diagram of the ionic liquid $[\text{mim}][\text{NTf}_2]$ + benzene reveals an equimolar inclusion compound with congruent melting temperature and its X-ray structure shows the formation of tube-like structures of benzene around the ionic liquid ions.

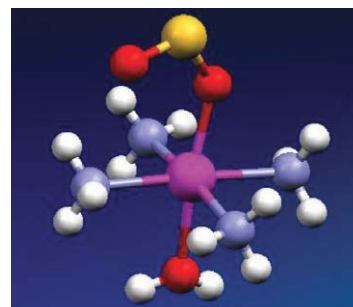


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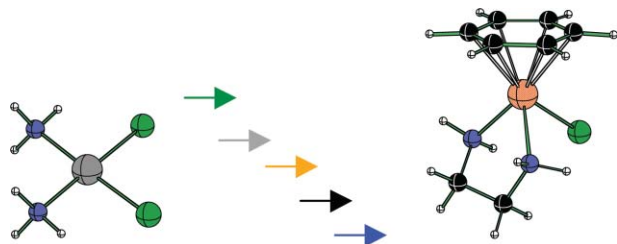
Photocrystallographic structure determination of a new geometric isomer of $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\eta^1\text{-OSO})][\text{MeC}_6\text{H}_4\text{SO}_3]_2$

Katharine F. Bowes, Jacqueline M. Cole,* Shamus L. G. Husheer, Paul R. Raithby,* Teresa L. Savarese, Hazel A. Sparkes, Simon J. Teat and John E. Warren

Photocrystallographic techniques have been used to determine the crystal structure of the metastable η^1 -OSO linkage isomer of the $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_2)]^{2+}$ cation.



2451

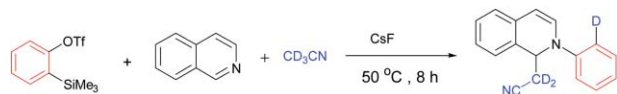


In silico evolution of substrate selectivity: comparison of organometallic ruthenium complexes with the anticancer drug cisplatin

Dirk V. Deubel* and Justin Kai-Chi Lau

A comparative quantum chemical approach helps to clarify how the selectivity of anticancer metallopharmaceuticals towards potential biological targets can be controlled by metal and ligands.

2454

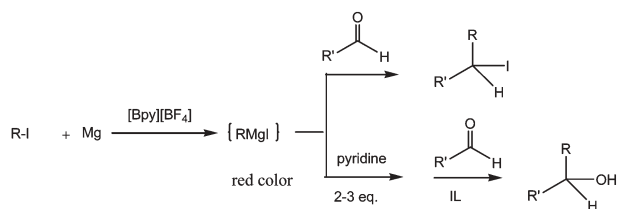


Reaction of arynes, *N*-heteroaromatics and nitriles

Masilamani Jeganmohan and Chien-Hong Cheng*

Various *N*-heteroaromatic compounds, including pyridines, quinolines and isoquinoline, react with arynes and nitrile-containing solvents to give *N*-arylated 1,2-dihydro-2-pyridinyl, -2-quinolinyl and -1-isoquinolinyl nitriles in excellent yields.

2457

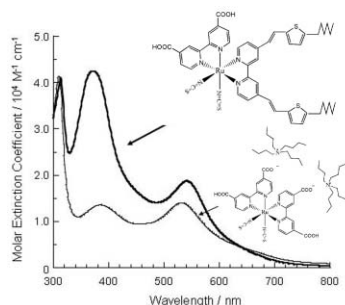


Grignard reagents in ionic liquids

Man Chun Law, Kwok-Yin Wong and Tak Hang Chan*

Grignard reagents were generated for the first time from magnesium and organic iodides in the ionic liquid *n*-butylpyridinium tetrafluoroborate, [bpy][BF₄], and they showed different reactivity from classical Grignard reagents in organic solvents.

2460



A novel ruthenium sensitizer with a hydrophobic 2-thiophen-2-yl-vinyl-conjugated bipyridyl ligand for effective dye sensitized TiO₂ solar cells

Ke-Jian Jiang, Naruhiko Masaki, Jiang-bin Xia, Shuji Noda and Shozo Yanagida*

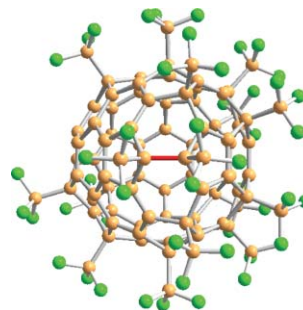
The novel 2-thiophen-2-yl-vinyl conjugated ruthenium sensitizer (HRS-1) shows respectable light harvesting performance in the visible-light region, giving a higher solar light-to-electricity conversion efficiency compared to the N719 sensitizer under comparable conditions.

2463

Preparation, crystallographic characterization and theoretical study of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$

Stanislav M. Avdoshenko, Alexey A. Goryunkov, Ilya N. Ioffe, Daria V. Ignat'eva, Lev N. Sidorov, Philip Pattison, Erhard Kemnitz and Sergey I. Troyanov*

$C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$ are the first CF_3 fullerene derivatives to comprise a pair of adjacent CF_3 groups. They have been isolated from a mixture obtained *via* reaction of C_{70} with CF_3I , characterized in a single crystal XRD study and theoretically investigated at the DFT level of theory.

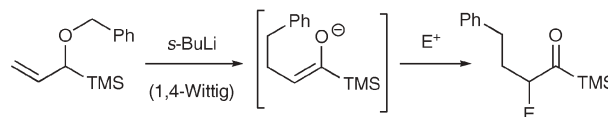


2466

α -Substituted acylsilanes *via* a highly selective [1,4]-Wittig rearrangement of α -benzyloxyallylsilane

Edith N. Onyeozili and Robert E. Maleczka Jr.*

After deprotonation with *s*-BuLi at cold temperatures, α -benzyloxyallylsilane undergoes [1,4]-Wittig rearrangement with unprecedented selectivity to give an enolate that can be used to generate a variety of acylsilanes.

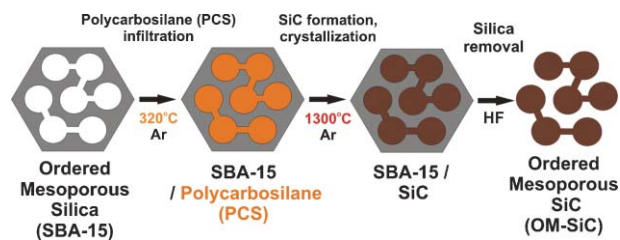


2469

Ordered mesoporous silicon carbide (OM-SiC) *via* polymer nanocasting

Piotr Krawiec, Dorin Geiger and Stefan Kaskel*

Ordered mesoporous SiC with high specific surface area ($650\text{--}800\text{ m}^2\text{ g}^{-1}$) and well ordered pore structure was obtained *via* nanocasting of polycarbosilanes into ordered mesoporous silica SBA-15 and subsequent conversion of the polymer at $1300\text{ }^\circ\text{C}$.

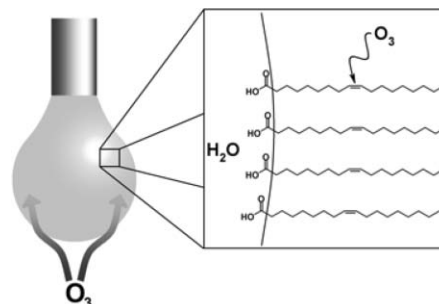


2471

Real-time monitoring of the ozonolysis of unsaturated organic monolayers

Erick González-Labrada, Rolf Schmidt and Christine E. DeWolf*

The reaction of ozone with unsaturated organic molecules at the air–water interface of a pendant drop was followed by axisymmetric drop shape analysis (ADSA).



2474

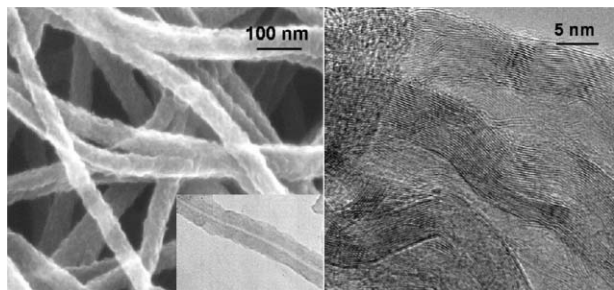


The direct reaction of the *t*Bu-DAB ligand with SeCl₄: a redox route to selenium–nitrogen heterocycles

Jason L. Dutton, Jocelyn J. Tindale, Michael C. Jennings and Paul J. Ragonna*

The reaction of SeCl₄ with the ubiquitous *tert*-butyl-substituted diazabutadiene ligand results in the isolation of a rare example of a 1,2,5-selenadiazolium cation, representing a novel route to Se–N ring formation. These heterocycles can be derivatised at selenium, which has led to the identification of a short Se···N secondary bonding interaction.

2477

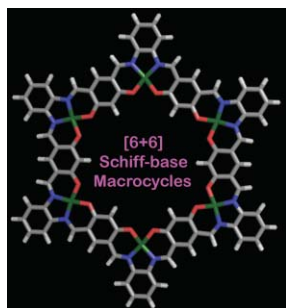


Microwave synthesis of nanocarbons from conducting polymers

Xinyu Zhang and Sanjeev K. Manohar*

Bulk quantities of nanocarbons having pre-selected morphology can be synthesized, rapidly, and in one step, by heating doped conducting polymer precursors having similar morphology in a microwave oven, where the precursors' bulk morphology is retained upon microwave heating (spheres, fibers, tubes).

2480

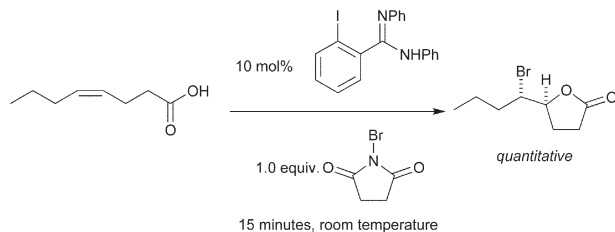


[6 + 6] Schiff-base macrocycles with 12 imines: giant analogues of cyclohexane

Joseph K.-H. Hui and Mark J. MacLachlan*

The Schiff-base condensation reaction of 12 components in solution has yielded large hexagon-shaped conjugated macrocycles with 6 N₂O₂ coordination sites.

2483



Ortho-substituted iodobenzenes as novel organocatalysts for bromination of alkenes

D. Christopher Braddock,* Gemma Cansell and Stephen A. Hermitage

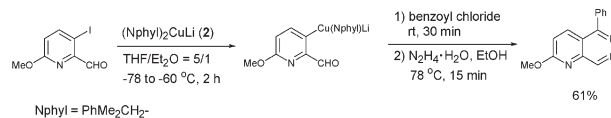
Suitably *ortho*-substituted iodobenzenes act as catalysts for the transfer of electrophilic bromine from *N*-bromosuccinimide to alkenes as exemplified by the bromolactonisation of unsaturated aliphatic carboxylic acids.

2486

Direct preparation of copper organometallics bearing an aldehyde function *via* an iodine–copper exchange

Xiaoyin Yang and Paul Knochel*

The iodine–copper exchange reaction allows the direct preparation of various aryl, heteroaryl and alkenyl cuprates bearing a formyl group, thus allowing a direct synthesis of polyfunctional aldehydes without the need of protecting groups or an additional oxidation step.

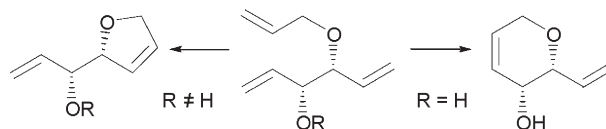


2489

Control of ring size selectivity by substrate directable RCM

Bernd Schmidt* and Stefan Nave

The presence or absence of a hydroxy protecting group determines the ring size selectivity of an RCM reaction. This observation suggests that hydroxy groups may exert strong catalytic-directing effects in olefin metathesis reactions.

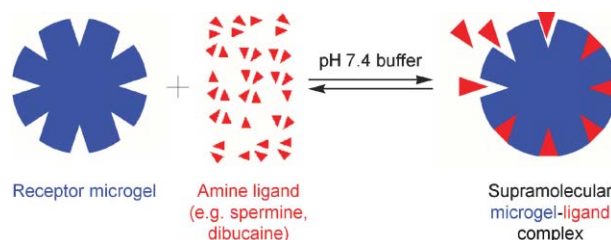


2492

Supramolecular binding of protonated amines to a receptor microgel in aqueous medium

Alan Tominey, David Andrew, Lewis Oliphant, Georgina M. Rosair, Juliette Dupré and Arno Kraft*

Polyanionic microgels containing negatively charged tetrazole binding sites were synthesised and showed supramolecular binding of various protonated amines (*e.g.* dibucaine, propranolol, spermine) in a competitive aqueous medium at millimolar concentration.

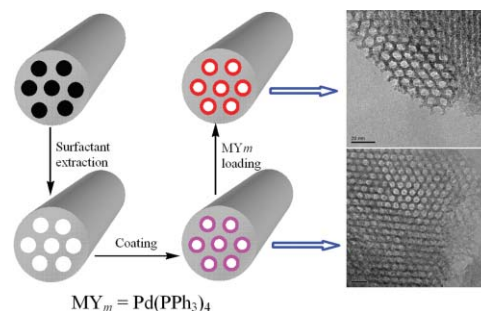


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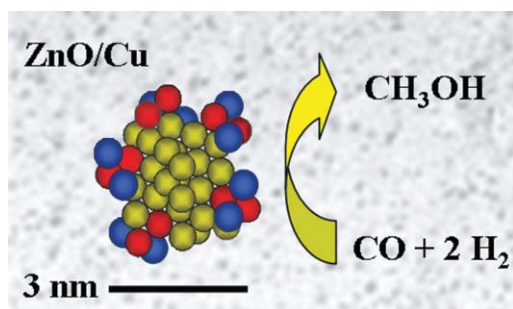
A water-compatible, highly active and reusable PEG-coated mesoporous silica-supported palladium complex and its application in Suzuki coupling reactions

Qing Yang, Shengming Ma,* Jixue Li, Fengshou Xiao* and Hai Xiong

An air stable heterogeneous palladium catalyst, prepared from a coated mesoporous material containing a layer of PEG, showed very high catalytic activity for aqueous Suzuki coupling reactions.



2498

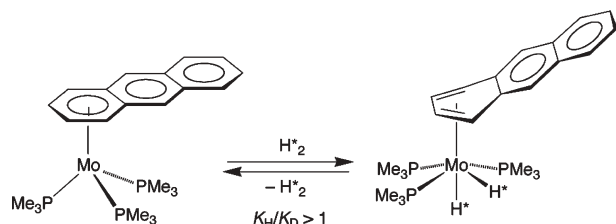


A colloidal ZnO/Cu nanocatalyst for methanol synthesis

Marie Katrin Schröter, Lamma Khodeir, Maurits W. E. van den Berg, Todor Hikov, Mirza Cokoja, Shaojun Miao, Wolfgang Grünert, Martin Muhler and Roland A. Fischer*

Free-standing, ZnO surface decorated Cu nanoparticles of 1–3 nm in size form stable colloids in squalane and proved to be highly active quasi homogeneous catalysts for methanol synthesis from CO and H₂.

2501

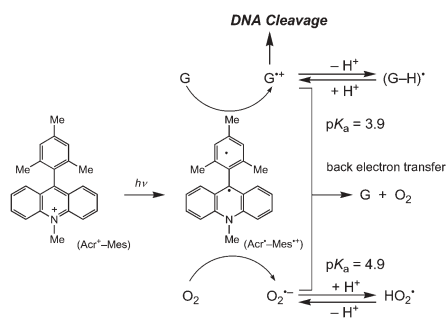


A normal equilibrium isotope effect for oxidative addition of H₂ to (η^6 -anthracene)Mo(PMe₃)₃

Guang Zhu, Kevin E. Janak and Gerard Parkin*

Oxidative addition of H₂ and D₂ to the anthracene complex (η^6 -AnH)Mo(PMe₃)₃ giving (η^4 -AnH)Mo(PMe₃)₃X₂ (X = H, D) is characterized by a normal equilibrium isotope effect ($K_{\text{H}}/K_{\text{D}} > 1$) at temperatures close to ambient, in marked contrast to the inverse values that have been previously reported for other oxidative addition reactions.

2504

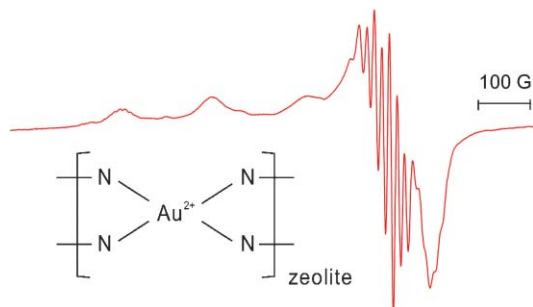


Direct detection of nucleotide radical cations produced by electron-transfer oxidation of DNA bases with electron-transfer state of 9-mesityl-10-methylacridinium ion and resulting efficient DNA cleavage without oxygen

Kei Ohkubo, Kazusa Yukimoto and Shunichi Fukuzumi*

Photoinduced electron transfer of DNA as well as DNA bases with 9-mesityl-10-methylacridinium ion results in formation of all types of DNA base radical cations, which have been detected as the transient absorption spectra in the laser flash photolysis measurements, leading to efficient DNA cleavage in the absence of O₂.

2507



ESR observation of the formation of an Au(II) complex in zeolite Y

Zhenping Qu, Liviu Giurgiu and Emil Roduner*

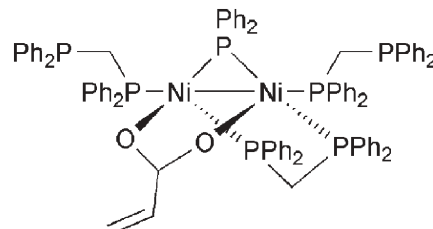
First time observation of an Au(II) complex stabilized in a zeolite Y supercage, as evidenced by electron spin resonance (ESR). Confinement in the zeolite pores obviously prevents this unusual oxidation state from undergoing disproportionation.

2510

A key step in the formation of acrylic acid from CO₂ and ethylene: the transformation of a nickelalactone into a nickel-acrylate complex

Reinald Fischer, Jens Langer, Astrid Malassa,
Dirk Walther,* Helmar Görls and Gavin Vaughan

The reaction of a nickelalactone with dppm, resulting in an acrylate-bridged binuclear Ni(I) complex, models a key step in the formation of acrylic acid from CO₂ and ethylene.



Chemical Biology: Directing Biosynthesis

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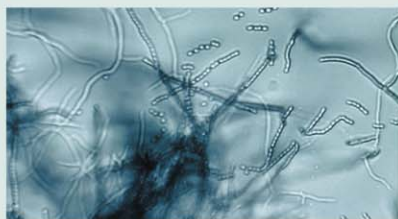
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AUTHOR INDEX

- Anderson, Paul A., 2439
Andrew, David, 2492
Avdoshenko, Stanislav M., 2463
Bento, Isabel, 2445
Bowes, Katharine F., 2448
Braddock, D. Christopher, 2483
Cansell, Gemma, 2483
Chan, Tak Hang, 2457
Chater, Philip A., 2439
Cheng, Chien-Hong, 2454
Cokoja, Mirza, 2498
Cole, Jacqueline M., 2448
Coleman, Anthony W., 2425
David, William I. F., 2439
Deubel, Dirk V., 2451
DeWolf, Christine E., 2471
Duarte, M. Teresa, 2445
Dupr e, Juliette, 2492
Dutton, Jason L., 2474
Edwards, Peter P., 2439
Fischer, Reinald, 2510
Fischer, Roland A., 2498
Fukuzumi, Shunichi, 2504
Geiger, Dorin, 2469
Giurgiu, Liviu, 2507
Gonz alez-Labrada, Erick, 2471
G orls, Helmar, 2510
Goryunkov, Alexey A., 2463
Gr unert, Wolfgang, 2498
Hermitage, Stephen A., 2483
Hikov, Todor, 2498
Hui, Joseph K.-H., 2480
Husheer, Shamus L. G., 2448
Ignat'eva, Daria V., 2463
Ioffe, Ilya N., 2463
Janak, Kevin E., 2501
Jeganmohan, Masilamani, 2454
Jennings, Michael C., 2474
Jiang, Ke-Jian, 2460
Johnson, Simon R., 2439
Kaskel, Stefan, 2469
Kemnitz, Erhard, 2463
Khodeir, Lamma, 2498
Kimizuka, Nobuo, 2442
Knochel, Paul, 2486
Kraft, Arno, 2492
Krawiec, Piotr, 2469
Kume, Shoko, 2442
Kuroiwa, Keita, 2442
 achwa, Joanna, 2445
Langer, Jens, 2510
Lau, Justin Kai-Chi, 2451
Law, Man Chun, 2457
Lazar, Adina N., 2425
Li, Jixue, 2495
Lopes, Jos e N. Canongia, 2445
Ma, Shengming, 2495
MacLachlan, Mark J., 2480
Malassa, Astrid, 2510
Maleczka Jr., Robert E., 2466
Manohar, Sanjeev K., 2477
Masaki, Naruhiko, 2460
Miao, Shaojun, 2498
Muhler, Martin, 2498
Nave, Stefan, 2489
Noda, Shuji, 2460
Ohkubo, Kei, 2504
Oliphant, Lewis, 2492
Onyeozili, Edith N., 2466
Parkin, Gerard, 2501
Pattison, Philip, 2463
Perret, Florent, 2425
Qu, Zhenping, 2507
Ragogna, Paul J., 2474
Raithby, Paul R., 2448
Rebelo, Lu s P. N., 2445
Roduner, Emil, 2507
Rosair, Georgina M., 2492
Savarese, Teresa L., 2448
Schmidt, Bernd, 2489
Schmidt, Rolf, 2471
Schr oter, Marie Katrin, 2498
Sidorov, Lev N., 2463
Sparkes, Hazel A., 2448
Teat, Simon J., 2448
Tindale, Jocelyn J., 2474
Tominey, Alan, 2492
Trojanov, Sergey I., 2463
van den Berg, Maurits W. E., 2498
Vaughan, Gavin, 2510
Walther, Dirk, 2510
Warren, John E., 2448
Wong, Kwok-Yin, 2457
Xia, Jiang-bin, 2460
Xiao, Fengshou, 2495
Xiong, Hai, 2495
Yanagida, Shozo, 2460
Yang, Qing, 2495
Yang, Xiaoyin, 2486
Yukimoto, Kazusa, 2504
Zhang, Xinyu, 2477
Zhu, Guang, 2501

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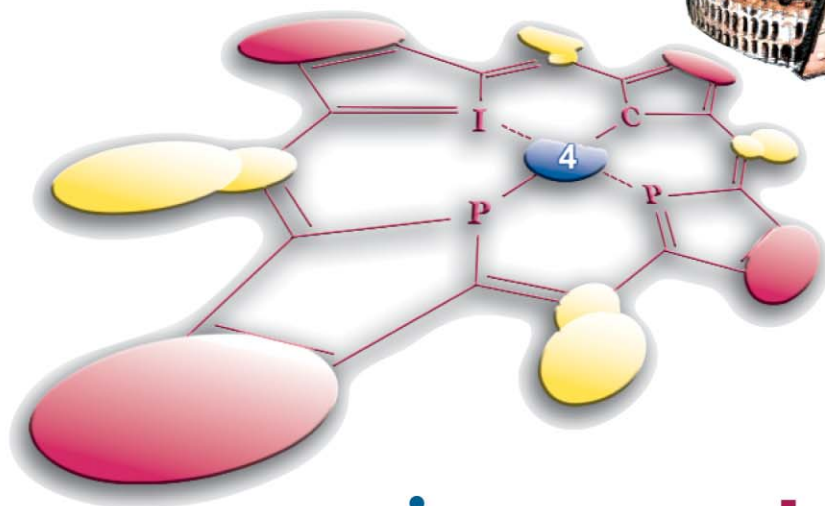
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