PERSPECTIVE

2144
On the existence of and mechanism for microwave-specific reaction rate enhancement
Gregory B. Dudley, Ranko Richert and A. E. Stiegman*

Microwave-specific chemical rate enhancement originates from the selective heating and accumulation of energy by solvated dipolar molecules in solution.

MINIREVIEWS

2153
Palladium: a future key player in the nanomedical field?
Anaëlle Dumas and Patrick Couvreur*

Palladium nanostructures with therapeutic potential are emerging as innovative tools in the nanomedical field.
Molecular engineering of mechanophore activity for stress-responsive polymeric materials
Cameron L. Brown and Stephen L. Craig*

Molecular-level design principles by which to engineer enhanced mechanophore activity are reviewed, with an emphasis on quantitative structure–activity studies determined for a family of gem-dihalocyclopropane mechanophores.

Label-free luminescence switch-on detection of hepatitis C virus NS3 helicase activity using a G-quadruplex-selective probe
Ka-Ho Leung, Hong-Zhang He, Bingsong He, Hai-Jing Zhong, Sheng Lin, Yi-Tao Wang, Dik-Lung Ma* and Chung-Hang Leung*

A novel luminescent G-quadruplex-selective iridium(III) complex was employed in a label-free G-quadruplex-based detection assay for hepatitis C virus NS3 helicase activity.

Bypassing the lack of reactivity of endo-substituted norbornenes with the catalytic rectification–insertion mechanism
Basile Commarieu and Jerome P. Claverie*

The novel rectification–insertion mechanism for the polymerization of polar norbornenes: making alternating copolymers from a single monomer.

Bioorthogonal oxime ligation mediated in vivo cancer targeting
Li Tang, Qian Yin, Yunxiang Xu, Qin Zhou, Kaimin Cai, Jonathan Yen, Lawrence W. Dobrucki and Jianjun Cheng*

Here, we report an in vivo cancer targeting strategy mediated by bioorthogonal oxime ligation.
Interconvertible multiple photoluminescence color of a gold(i) isocyanide complex in the solid state: solvent-induced blue-shifted and mechano-responsive red-shifted photoluminescence

Tomohiro Seki, Taichi Ozaki, Takuma Okura, Kiyotaka Asakura, Aya Sakon, Hidehiro Uekusa* and Hajime Ito*

We report the first example of a mechanochromic compound that can switch between four individual types of photoluminescence in the solid state.

Enantioselective cis-β-lactam synthesis by intramolecular C–H functionalization from enoldiazooacetamides and derivative donor–acceptor cyclopropenes

Xinfang Xu,* Yongming Deng, David N. Yim, Peter Y. Zavalij and Michael P. Doyle*

β-Lactam derivatives are produced through donor–acceptor cyclopropene intermediates in high yield with exclusive cis-diastereoselectivity, and high enantiocontrol.

Steric effects and quantum interference in the inelastic scattering of NO(X) + Ar

B. Nichols, H. Chadwick, S. D. S. Gordon, C. J. Eyles, B. Hornung, M. Brouard,* M. H. Alexander, F. J. Aoiz, A. Gijsbertsen and S. Stolte

New measurements of the differential steric effect for NO + Ar inelastic scattering highlight the importance of quantum interference.

Redefining q: quaternary ammonium cross sectional area (XSA) as a general descriptor for transport-limiting PTC rate approximations

S. E. Denmark* and J. J. Henle

Several descriptors were studied in transport-rate limiting PTC, with amphiphilic cross-sectional area (XSA) identified as a single-descriptor model of rate.
**EDGE ARTICLES**

**2219**

**Large ring-forming alkylations provide facile access to composite macrocycles**

Tristan E. Rose, Kenneth V. Lawson and Patrick G. Harran*

Friedel–Crafts cinnamylation can form unique and varied macrocycles with unmatched ease and functional group tolerance.

**2224**

**Plasmonic giant quantum dots: hybrid nanostructures for truly simultaneous optical imaging, photothermal effect and thermometry**

N. S. Karan, A. M. Keller, S. Sampat, O. Roslyak, A. Arefin, C. J. Hanson, J. L. Casson, A. Desirerddy, Y. Ghosh, A. Piryatinski, R. Iyer, H. Htoon, A. V. Malko and J. A. Hollingsworth*

A new compact and multifunctional hybrid semiconductor–metal nanostructure is elucidated and demonstrated for real-time optical imaging, photothermal heating, and in situ thermometry.

**2237**

**Photoinduced dynamics of a cyanine dye: parallel pathways of non-radiative deactivation involving multiple excited-state twisted transients**

Srigokul Upadhyayula, Vicente Nuñez, Eli M. Espinoza, Jillian M. Larsen, Duoduo Bao, Dewen Shi, Jenny T. Mac, Bahman Anvari and Valentine I. Vullev*

A photoexcited cyanine dye deactivates via multiple non-radiative pathways, only one of which is principally responsible for quenching its fluorescence.

**2252**

**Thermodynamics and kinetics of DNA nanotube polymerization from single-filament measurements**

Rizal F. Hariadi, Bernard Yurke and Erik Winfree*

Single-filament measurement of the thermodynamic and kinetic parameters of DNA nanotube assembly supports a polymerization/depolymerization model sharing common features with cytoskeletal polymer models.
Thermal and optical control of electronic states in a single layer of switchable paramagnetic molecules

Giordano Poneti,* Lorenzo Poggini, Matteo Mannini,* Brunetto Cortigiani, Lorenzo Sorace, Edwige Otero, Philippe Saintctavit, Agnese Magnani, Roberta Sessoli and Andrea Dei

Thermally and optically induced Valence Tautomeric interconversion has been observed for a monolayer of a cobalt–dioxolene complex on gold.

Rhodium-catalyzed C–H functionalization-based approach to eight-membered lactams

Shangze Wu, Rong Zeng, Chunling Fu, Yihua Yu, Xue Zhang* and Shengming Ma*

Fused tricyclic skeleton in one shot: a RhIII catalyzed formal [4 + 2 + 2] cyclization of N-pivaloyloxybenzamides 1 with 1,6-allene-enes 2 adding two cycles to the benzene ring compatible with ambient air and moisture with a tolerance of many synthetic useful functional groups at room temperature have been developed.

Exploiting parameter space in MOFs: a 20-fold enhancement of phosphate-ester hydrolysis with UiO-66-NH2

Michael J. Katz, Su-Young Moon, Joseph E. Mondloch, M. Hassan Beyzavi, Casey J. Stephenson, Joseph T. Hupp* and Omar K. Farha*

Using the enzymatic mechanism of phosphoesterase as a template, we were able to modify a metal–organic framework such that the hydrolysis rates were 50 times faster than previously demonstrated with UiO-66.

A catalytic chiral gel microfluidic reactor assembled via dynamic covalent chemistry

Haoliang Liu, Juan Feng, Jianyong Zhang,* Philip W. Miller,* Liuping Chen and Cheng-Yong Su*

A novel dynamic covalent gel strategy is reported to immobilize an asymmetric catalyst within the channels of a microfluidic flow reactor.
EDGE ARTICLES

2297

Task-specific ionic liquid and CO2-cocatalysed efficient hydration of propargylic alcohols to \(\alpha\)-hydroxy ketones

Yanfei Zhao, Zhenzhen Yang, Bo Yu, Hongye Zhang, Huanjun Xu, Leiduan Hao, Buxing Han and Zhimin Liu*

Task-specific ionic liquid and CO2-cocatalysed efficient hydration of propargylic alcohols to \(\alpha\)-hydroxy ketones.

2302

Extreme red shifted SERS nanotags

Matthew A. Bedics, Hayleigh Kearns, Jordan M. Cox, Sam Mabbott, Fatima Ali, Neil C. Shand, Karen Faulds, Jason B. Benedict, Duncan Graham* and Michael R. Detty*

Extreme red-shifted nanotags have been developed and they provide effective SERS with picomolar detection limits when excited at 1280 nm.

2307

Tandem trimer pyrrole–imidazole polyamide probes targeting 18 base pairs in human telomere sequences

Yusuke Kawamoto, Asuka Sasaki, Kaori Hashiya, Satoru Ide, Toshikazu Bando,* Kazuhiro Maeshima* and Hiroshi Sugiyama*

The novel tandem trimer pyrrole-imidazole polyamide probe targeting 18 bp in telomeric repeats visualized telomeres in human cells selectively.

2313

Flaws in foldamers: conformational uniformity and signal decay in achiral helical peptide oligomers

Bryden A. F. Le Bailly, Liam Byrne, Vincent Diemer, Mohammadali Foroozandeh, Gareth A. Morris and Jonathan Clayden*

The conformational influence of a single stereogenic centre in an otherwise achiral oligomer behaves as a signal that decays with distance.
Successive light-induced two electron transfers in a Ru–Fe supramolecular assembly: from Ru–Fe(II)–OH₂ to Ru–Fe(IV)–oxo
C. Herrero, A. Quaranta, M. Sircoglou, K. Sénéchal-David, A. Baron, I. Marin, C. Buron, J.-P. Baltaze, W. Leibl,* A. Aukauloo* and F. Banse*
A Ru<sup>II</sup>–Fe<sup>II</sup> chromophore–catalyst assembly performs the visible-light activation of a metal-bound water molecule to form a metal oxo species responsible for the oxidation of a substrate.

Magnetic anisotropy of endohedral lanthanide ions: paramagnetic NMR study of MSc₂N@C₈₀−I₈ with M running through the whole 4f row
Y. Zhang, D. Krylov, M. Rosenkranz, S. Schiemenz and A. A. Popov*
Paramagnetic and variable temperature <sup>13</sup>C and <sup>45</sup>Sc nuclear magnetic resonance studies are performed for nitride clusterfullerenes MSc₂N@C₈₀ with icosahedral I₈(7) carbon cage, where M runs through all lanthanides forming nitride clusters.

Ruthenium-caged antisense morpholinos for regulating gene expression in zebrafish embryos
Julianne C. Griepenburg, Teresa L. Rapp, Patrick J. Carroll, James Eberwine and Ivan J. Dmochowski*
Ruthenium photolinkers provide a versatile method of using visible light to control structure and function of biopolymers.

Modulation of inherent dynamical tendencies of the bisabolyl cation via preorganization in epi-isozizaene synthase
Ryan P. Pemberton, Krystina C. Ho and Dean J. Tantillo*
The relative importance of various factors controlling the product distribution for a terpene synthase are elucidated through a combination of quantum chemical, dynamics and automated docking calculations.
Highly bent crystals formed by restrained π-stacked columns connected via alkyene linkers with variable conformations

Chih-Ming Chou, Shunpei Nobusue, Shohei Saito,* Daishi Inoue, Daisuke Hashizume and Shigehiro Yamaguchi*

Highly bent organic crystals are reproducibly prepared using a structurally restrained macrocyclic π-conjugated system with two flexible linkers. The appropriate length of the linkers to produce a void within the macrocycle is key to the observed bending of the crystals.

Engineering a FRET strategy to achieve a ratiometric two-photon fluorescence response with a large emission shift and its application to fluorescence imaging

Lin Yuan,* Fangping Jin, Zebing Zeng,* Chengbin Liu, Shenglian Luo and Jishan Wu

A FRET strategy was applied to develop a ratiometric two-photon fluorescent probe with a large emission shift for imaging in cells and tissues.

N-Heterocyclic carbene catalysed redox isomerisation of esters to functionalised benzaldehydes

Lisa Candish, Alison Levens and David W. Lupton*

N-Heterocyclic carbene catalysed redox isomerisation with reduction about the carbonyl has been developed in the transformation of trienyl esters to tetrasubstituted benzaldehydes.

Dynamical effects on the magnetic properties of dithiazolyl bistable materials

Sergi Vela, Mercé Deumal, Motoyuki Shiga, Juan J. Novoa and Jordi Ribas-Arino*

Using 1,3,5-trithia-2,4,6-triazapentalenylic material as a proof of concept, we demonstrate that vibrations of radicals can play a prime role in defining the magnetic properties of certain organic magnets.
Development of solvent-free synthesis of hydrogen-bonded supramolecular polyurethanes
Kelly, A. Houton, George M. Burslem and Andrew. J. Wilson*
A solvent free ball-milling method for the synthesis of small molecule and oligomeric carbamates is described that is applicable to supramolecular polymer synthesis.

Unravelling the correlation between metal induced aggregation and cellular uptake/subcellular localization of ZnSalen: an overlooked rule for design of luminescent metal probes
Juan Tang, Yuan-Bo Cai, Jing Jing and Jun-Long Zhang*
We demonstrate the importance of speciation of luminescent metal complexes in water on biological behaviours such as cellular uptake and subcellular localization.

Competitive formation of homocircuit [3]rotaxanes in synthetically useful yields in the bipyridine-mediated active template CuAAC reaction
Edward A. Neal and Stephen M. Goldup*
We demonstrate that, depending on reaction conditions, [2]rotaxanes are produced in essentially quantitative yield in the AT-CuAAC reaction regardless of macrocycle size, and hard to access doubly threaded [3]rotaxanes can be synthesised in up to 50% isolated yield in a four component coupling step.

Rapid water oxidation electrocatalysis by a ruthenium complex of the tripodal ligand tris(2-pyridyl)phosphine oxide
Andrew G. Walden and Alexander J. M. Miller*
A ruthenium complex of the tripodal ligand tris(2-pyridyl)phosphine oxide exhibits rapid water oxidation electrocatalysis over a wide pH range.
**EDGE ARTICLES**

2411

Long-range two-photon scattering spectroscopy ruler for screening prostate cancer cells

Sudarson Sekhar Sinha, Dilip K. Paul, Rajashekhar Kanchanapally, Avijit Pramanik, Suhash Reddy Chavva, Bhanu Priya Viraka Nellore, Stacy J. Jones and Paresh Chandra Ray*

Development of a long-range TPS ruler for the screening of prostate cancer cells with sensitivity of 5 cells per mL level is demonstrated.

2419

Two-photon sensitive protecting groups operating via intramolecular electron transfer: uncaging of GABA and tryptophan

Karolina A. Korzycka, Philip M. Bennett, Eduardo Jose Cueto-Diaz, Geoffrey Wicks, Mikhail Drobizhev, Mireille Blanchard-Desce, Aleksander Rebane and Harry L. Anderson*

We present a modular approach to photo-labile protecting groups based on photoinduced electron transfer, providing high sensitivity to two-photon excitation.

2427

Phenalenyl-fused porphyrins with different ground states

Wangdong Zeng, Sangsu Lee, Minjung Son, Masatoshi Ishida, Ko Furukawa, Pan Hu, Zhe Sun, Dongho Kim* and Jishan Wu*

Fusion of one or two phenalenyl units onto the porphyrin core led to biradicaloids with different ground state, physical property and chemical reactivity.

2434

Stereocontrolled protein surface recognition using chiral oligoamide proteomimetic foldamers

Valeria Azzarito, Jennifer A. Miles, Julie Fisher, Thomas A. Edwards, Stuart L. Warriner and Andrew J. Wilson*

An oligoamide helix mimicking foldamer with well-defined conformation is shown to recognize its target protein hDM2 in a manner that depends upon the composition, spatial projection and stereochemistry of functional groups appended to the scaffold.
Self-assembled trinuclear arsenic and antimony macrobicycles

Mary S. Collins, Robert Y. Choi, Lev N. Zakharov, Lori A. Watson, Benjamin P. Hay and Darren W. Johnson*

Six new macrobicyclic Pn3L2Cl3 complexes (Pn = As, Sb) were synthesized by self-assembly of a three-fold symmetric trithiol and PnCl3.

Target profiling of an antimetastatic RAPTA agent by chemical proteomics: relevance to the mode of action

Maria V. Babak, Samuel M. Meier, Kilian V. M. Huber, Jónannes Reynisson, Anton A. Legin, Michael A. Jakupec, Alexander Roller, Alexey Stukalov, Manuela Gridling, Keiryn L. Bennett, Jacques Colinge, Walter Berger, Paul J. Dyson, Giulio Superti-Furga, Bernhard K. Kepl er and Christian G. Hartinger*

The RAPTA pharmacophore was linked to beads to identify its biomolecular targets in cancer cells.

Elucidating organ-specific metabolic toxicity chemistry from electrochemiluminescent enzyme/DNA arrays and bioreactor bead-LC-MS/MS

Dhanuka P. Wasalathanthri, Dandan Li, Donghui Song, Zhifang Zheng, Dharamainder Choudhary, Ingela Jansson, Xiuling Lu, John B. Schenkman and James F. Rusling*

Combining electrochemiluminescent array and bioreactor bead-LC-MS/MS featuring metabolic enzyme-DNA films provide an efficient, comprehensive approach to simultaneously elucidate metabolic DNA damage chemistries at different human organs for potential new drugs.

Graphene–DNAzyme junctions: a platform for direct metal ion detection with ultrahigh sensitivity

Li Gao, Le-Le Li, Xiaolong Wang, Peiwen Wu, Yang Cao, Bo Liang, Xin Li, Yuanwei Lin, Yi Lu* and Xuefeng Guo*

We describe a method of creating graphene–DNAzyme junctions capable of directly detecting paramagnetic Cu2+ with femtomolar sensitivity and high selectivity.
EDGE ARTICLES

2474
Re-evaluating the Cu K pre-edge XAS transition in complexes with covalent metal–ligand interactions

Neil C. Tomson,* Kamille D. Williams, Xuliang Dai, Stephen Sproules, Serena DeBeer, Timothy H. Warren* and Karl Wieghardt*

Covalent metal–ligand interactions can lead to Cu K pre-edge transitions that result from metal-to-ligand charge transfer, instead of $1s \rightarrow 3d$, character.

2488
Intermolecular carbene S–H insertion catalysed by engineered myoglobin-based catalysts

Vikas Tyagi, Rachel B. Bonn and Rudi Fasan*

The first example of a biocatalytic strategy for the synthesis of thioethers via an intermolecular carbene S–H insertion reaction is reported.

2495
Copper doped ceria porous nanostructures towards a highly efficient bifunctional catalyst for carbon monoxide and nitric oxide elimination

Shanlong Li, Nengli Wang, Yonghai Yue, Guangsheng Wang, Zhao Zu and Yu Zhang*

Cu$^{2+}$ doped CeO$_2$ porous nanomaterials were synthesized by calcining CeCu–MOF nanocrystals. They exhibited a superior bifunctional catalytic performance for CO oxidation and selective catalytic reduction of NO.

2501
Identifying lead hits in catalyst discovery by screening and deconvoluting complex mixtures of catalyst components

Eléna Wolf, Edward Richmond and Joseph Moran*

A combinatorial screening strategy is described that exploits complex mixtures of precatalysts and ligands to rapidly uncover lead in situ generated catalysts.
Extending $N$-heterocyclic carbene ligands into the third dimension: a new type of hybrid phosphazane/NHC system

Torsten Roth, Vladislav Vasilenko, Callum G. M. Benson, Hubert Wadepohl, Dominic S. Wright* and Lutz H. Gade*

A new type of hybrid phosph(III)azane/NHC system is described in which a phosphazane P$_2$N$_2$ ring provides unique opportunities for modifying the electronic and steric character of these carbenes.

Template- and surfactant-free synthesis of ultrathin CeO$_2$ nanowires in a mixed solvent and their superior adsorption capability for water treatment

Xiao-Fang Yu, Jian-Wei Liu, Hual-Ping Cong, Lei Xue, Muhammad Nadeem Arshad, Hassan A. Albar, Tariq R. Sobahi, Qiang Gao and Shu-Hong Yu*

Ultrathin CeO$_2$ nanowires can be prepared by a one-step refluxing approach in a mixed solvent without any templates or surfactants, and exhibit excellent adsorption capabilities in water treatment.

Tuning fluorocarbon adsorption in new isoreticular porous coordination frameworks for heat transformation applications

Rui-Biao Lin, Tai-Yang Li, Hao-Long Zhou, Chun-Ting He, Jie-Peng Zhang* and Xiao-Ming Chen

We report adsorption behaviors of a typical fluorocarbon R22 (CHClF$_2$) in a new series of isoreticular porous coordination frameworks [Zn$_4$O(bpz)$_2$(ldc)].

Turning it off! Disfavouring hydrogen evolution to enhance selectivity for CO production during homogeneous CO$_2$ reduction by cobalt–terpyridine complexes

Noémie Elgrishi, Matthew B. Chambers and Marc Fontecave*

Understanding the activity and selectivity of molecular catalysts for CO$_2$ reduction to fuels is an important scientific endeavour in addressing the growing global energy demand.
Computational study of the mechanism and selectivity of ruthenium-catalyzed hydroamidations of terminal alkynes

Bholanath Maity, Lukas J. Gooßen* and Debasis Koley*

Density functional theory calculations were performed to elucidate the mechanism of the ruthenium-catalyzed hydroamidation of terminal alkynes, a powerful and sustainable method for the stereoselective synthesis of enamides.

Mechanical and optical properties of ultralarge flakes of a metal–organic framework with molecular thickness

Cristina Hermosa, Benjamin R. Horrocks, José I. Martínez, Fabiola Liscio, Julio Gómez-Herrero* and Félix Zamora*

The red emission on isolated 2d-mof flakes with areas of square microns and molecular thicknesses (from single up to ca. 50 layers) has been characterized. Free-standing flakes have also been produced and their mechanical and optical properties studied.

Synthesis and reactivity of cyclo-tetra(stibinophosphonium) tetracations: redox and coordination chemistry of phosphine–antimony complexes

Saurabh S. Chitnis, Alasdair P. M. Robertson, Neil Burford,* Jan J. Weigand* and Roland Fischer

Reactions of trialkylphosphines with antimony(III) triflates yield catena-antimony(i) cations revealing a new reductive elimination/oxidative coupling reaction for P–Sb coordination complexes.

Pattern-based detection of anion pollutants in water with DNA polyfluorophores

Hyukin Kwon, Wei Jiang and Eric T. Kool*

Eight fluorescent DNA-like oligomers bound to Y(III) or Zn(II) and attached to microbeads were able to distinguish 17 anions at micromolar concentrations in water.
A dual-response BODIPY-based fluorescent probe for the discrimination of glutathione from cystein and homocystein

Feiyi Wang, Li Zhou, Chunchang Zhao,* Rui Wang, Qiang Fei, Sihang Luo, Zhiqian Guo, He Tian and Wei-Hong Zhu*

By employing a dual response approach, distinguishable fluorescence signals are initiated by GSH-mediated and Cys/Hcy-induced cascade reactions, thus allowing selective detection.

Enantioselective synthesis of D-α-amino amides from aliphatic aldehydes

Kenneth E. Schwieter and Jeffrey N. Johnston*

Bromonitromethane is used in a phase transfer-catalysed enantioselective aza-Henry reaction, leading to D-amino amide bearing an alkyl chain.

Controlled levels of protein modification through a chromatography-mediated bioconjugation

Richard L. Kwant, Jake Jaffe, Peter J. Palmere and Matthew B. Francis*

This article introduces a method to control levels of protein modification through a chromatography-mediated bioconjugation.

High-throughput imaging assay of multiple proteins via target-induced DNA assembly and cleavage

Chen Zong, Jie Wu, Mengmeng Liu, Feng Yan and Huangxian Ju*

A versatile imaging strategy integrated with target-induced DNA assembly and cleavage was designed for an assay for multiple proteins.
2608

A mechanically interlocked molecular system programmed for the delivery of an anticancer drug

Romain Barat, Thibaut Legigan, Isabelle Tranoy-Opalinski, Brigitte Renoux, Elodie Péraudeau, Jonathan Clarhaut, Pauline Poinot, Antony E. Fernandes, Vincent Aucagne, David A. Leigh and Sébastien Papot*

The development of mechanically interlocked molecular systems programmed to operate autonomously in biological environments is an emerging field of research with potential medicinal applications.

2614

Compact, hydrophilic, lanthanide-binding tags for paramagnetic NMR spectroscopy

M. D. Lee, C.-T. Loh, J. Shin, S. Chhabra, M. L. Dennis, G. Otting, J. D. Swarbrick* and B. Graham*

The design, synthesis and evaluation of four novel lanthanide-binding tags for paramagnetic NMR spectroscopy are reported.