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See V. P. Ananikov *et al.*,
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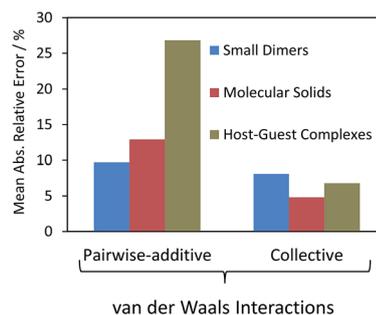
PERSPECTIVE

3289

van der Waals dispersion interactions in molecular materials: beyond pairwise additivity

Anthony M. Reilly and Alexandre Tkatchenko*

In this perspective we discuss recent advances in the understanding of collective and many-body van der Waals interactions and their role and impact for molecular materials.



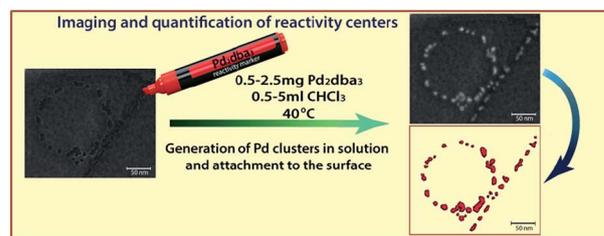
EDGE ARTICLES

3302

Spatial imaging of carbon reactivity centers in Pd/C catalytic systems

E. O. Pentsak, A. S. Kashin, M. V. Polynski, K. O. Kvashnina, P. Glatzel and V. P. Ananikov*

In the present study state-of-the-art experimental techniques involving ultra high resolution SEM/STEM microscopy (1 Å resolution), high brilliance X-ray absorption spectroscopy and theoretical calculations on truly nanoscale systems were utilized to reveal the role of carbon centers in the formation and nature of Pd/C catalytic materials.



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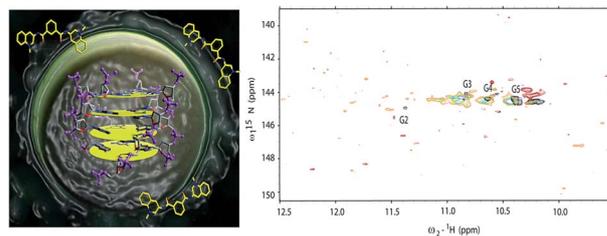


3314

G-quadruplex DNA and ligand interaction in living cells using NMR spectroscopy

Gilmar F. Salgado,* Christian Cazenave, Abdelaziz Kerkour and Jean-Louis Mergny

Using in-cell NMR spectroscopy to probe ligand binding to a G-quadruplex nucleic acid.

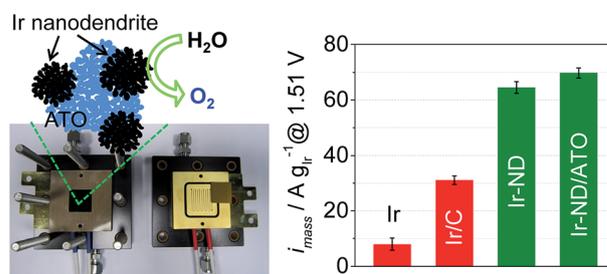


3321

Oxide-supported Ir nanodendrites with high activity and durability for the oxygen evolution reaction in acid PEM water electrolyzers

Hyung-Suk Oh, Hong Nhan Nong, Tobias Reier, Manuel Gliech and Peter Strasser*

Ir nanodendrites (Ir-ND) supported on antimony doped tin oxide (ATO) show enhanced catalytic activity and stability for oxygen evolution reaction (OER) in polymer electrolyte membrane (PEM) water electrolyzers.

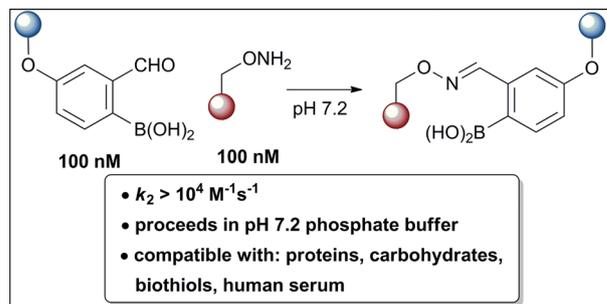


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Boronic acids facilitate rapid oxime condensations at neutral pH

Pascal Schmidt, Cedric Stress and Dennis Gillingham*

We report here the discovery and development of boron-assisted oxime formation as a powerful connective reaction for chemical biology.

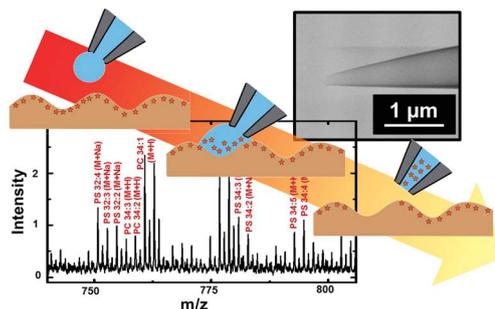


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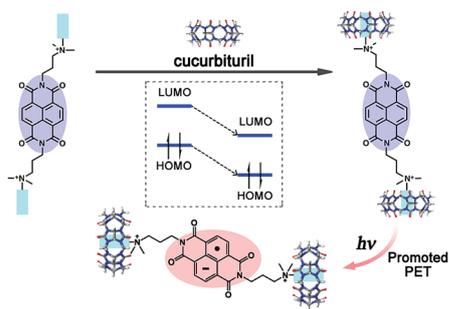
Nanopipettes: probes for local sample analysis

Anumita Saha-Shah, Anna E. Weber, Jonathan A. Karty, Steven J. Ray, Gary M. Hieftje and Lane A. Baker*

Nanopipettes are demonstrated as probes for local mass spectrometric analysis with potential for small-scale extraction of analytes from single cells, tissue and organisms.



3342

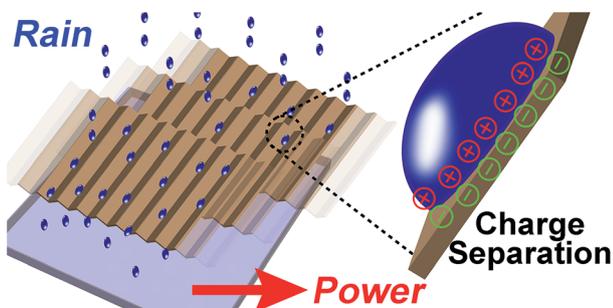


A supramolecular strategy for tuning the energy level of naphthalenediimide: Promoted formation of radical anions with extraordinary stability

Qiao Song, Fei Li, Zhiqiang Wang and Xi Zhang*

We report a supramolecular strategy to promote the formation of naphthalenediimide radical anions with extraordinary stability through tuning the energy level of naphthalenediimide.

3347



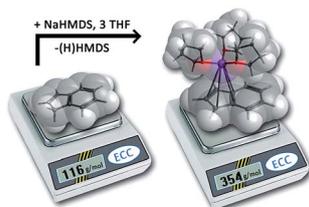
Using the gravitational energy of water to generate power by separation of charge at interfaces

Yajuan Sun, Xu Huang and Siowling Soh*

When water droplets (e.g., from rain) flow down a solid surface due to gravity, they can generate power.

3354

Molecular Weight Determination	Internal Calibration Curve (ICC)	External Calibration Curve (ECC)
Accurate MWs	✓	✓
High Temp-range	✓	✓
Reusable	✗	✓
One Internal Reference is sufficient	✗	✓
Easy Adjustment on Geometry	✗	✓
Normalized Diffusion Coefficients	✗	✓

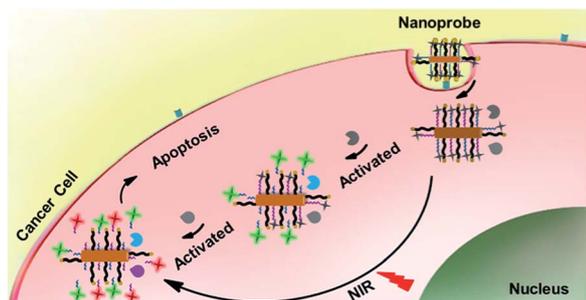


Accurate molecular weight determination of small molecules via DOSY-NMR by using external calibration curves with normalized diffusion coefficients

Roman Neufeld and Dietmar Stalke*

We describe a novel development of MW-determination by using an external calibration curve approach with normalized diffusion coefficients.

3365



In situ activation and monitoring of the evolution of the intracellular caspase family

Lei Zhang, Jianping Lei,* Jintong Liu, Fengjiao Ma and Huangxian Ju*

An integrated nano-platform is designed to achieve *in situ* activation, monitoring and signal feedback of the caspase family evolution from upstream to downstream.

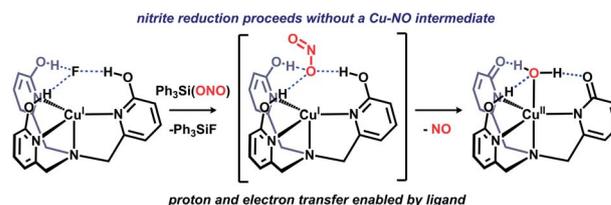


3373

Nitrite reduction by copper through ligand-mediated proton and electron transfer

Cameron M. Moore and Nathaniel K. Szymczak*

A copper complex featuring a proton-responsive tripodal ligand reduces nitrite *via* a proton/electron transfer process, which parallels copper nitrite reductase.

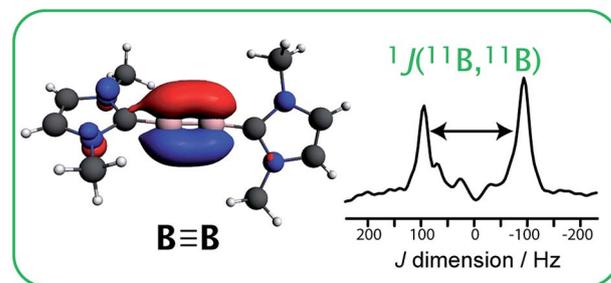


3378

Spying on the boron–boron triple bond using spin–spin coupling measured from ^{11}B solid-state NMR spectroscopy

Frédéric A. Perras, William C. Ewing, Theresa Dellermann, Julian Böhnke, Stefan Ullrich, Thomas Schäfer, Holger Braunschweig* and David L. Bryce*

Boron–boron J coupling constants provide new insight into the nature of the boron–boron triple bond.

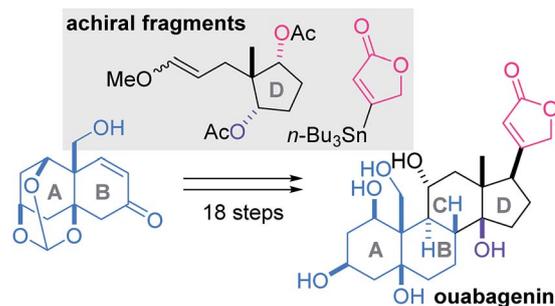


3383

A convergent total synthesis of ouabagenin

Ken Mukai, Satoshi Kasuya, Yuki Nakagawa, Daisuke Urabe and Masayuki Inoue*

A convergent total synthesis of ouabagenin, an aglycon of cardenolide glycoside ouabain, was achieved by assembly of the AB-ring, D-ring and butenolide moieties.

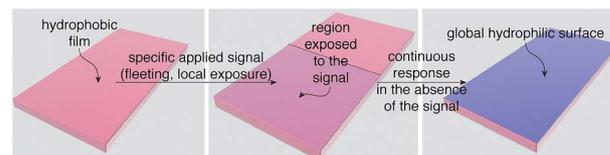


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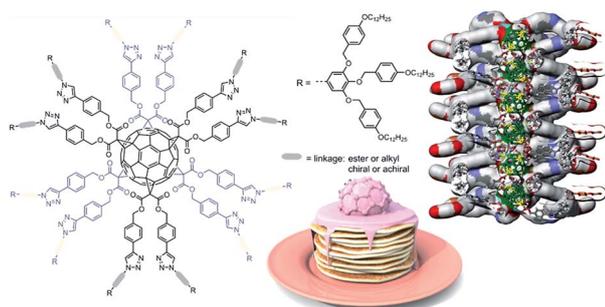
Polymeric materials that convert local fleeting signals into global macroscopic responses

Hyungwoo Kim, Matthew S. Baker and Scott T. Phillips*

Polymers that support self-propagating reactions are used to create materials that change global wetting properties in response to specific fleeting, local stimuli.



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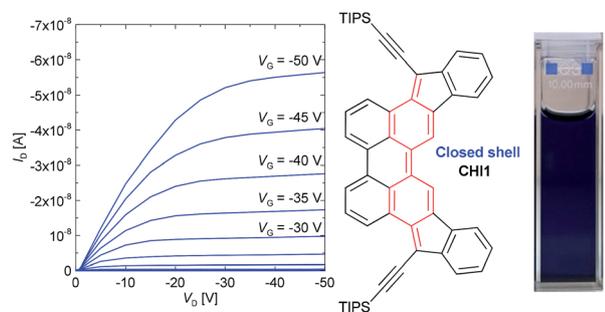


Self-organisation of dodeca-dendronized fullerene into supramolecular discs and helical columns containing a nanowire-like core

Sebastiano Guerra, Julien lehl, Michel Holler, Mihai Peterca, Daniela A. Wilson, Benjamin E. Partridge, Shaodong Zhang, Robert Deschenaux,* Jean-François Nierengarten* and Virgil Percec*

C_{60} dendronized with 12 chiral or achiral self-assembling dendrons form discs with C_{60} at their centre that self-organise into helical columns with a nanowire-like core.

3402

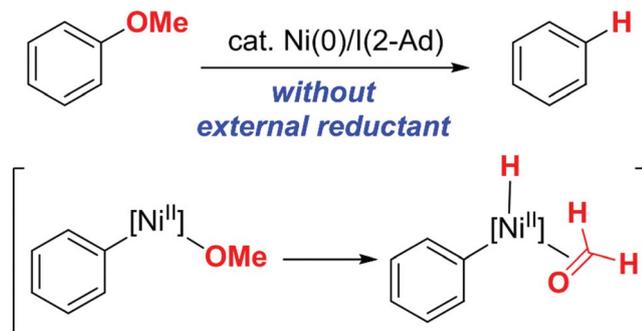


Diindeno[1,2-*b*:2',1'-*n*]perylene: a closed shell related Chichibabin's hydrocarbon, the synthesis, molecular packing, electronic and charge transport properties

Kamal Sbagoud, Masashi Mamada,* Jérôme Marrot, Shizuo Tokito, Abderrahim Yassar* and Michel Frigoli*

A fixed Chichibabin's hydrocarbon CHI1 shows a closed shell configuration with a broad absorption from 400 up to 900 nm.

3410

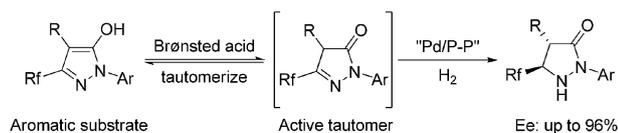


Nickel-catalyzed reductive cleavage of aryl alkyl ethers to arenes in absence of external reductant

Mamoru Tobisu,* Toshifumi Morioka, Akimichi Ohtsuki and Naoto Chatani*

A nickel catalyst for reductive cleavage of aryl ethers in the absence of an external reductant is developed. The alkoxy group of the substrate serves as an internal reductant.

3415



Pd-catalyzed asymmetric hydrogenation of fluorinated aromatic pyrazol-5-ols via capture of active tautomers

Zhang-Pei Chen, Mu-Wang Chen, Lei Shi, Chang-Bin Yu and Yong-Gui Zhou

Here we explore a novel strategy for asymmetric hydrogenation of aromatic pyrazol-5-ols via capture of the active tautomers.

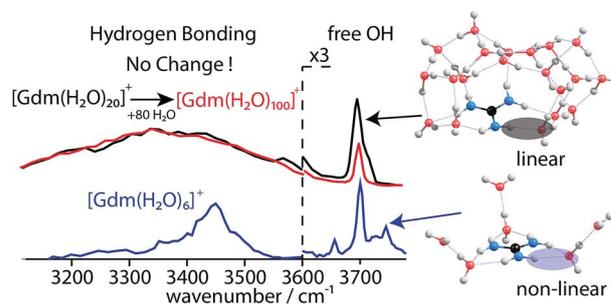


3420

Hydration of guanidinium depends on its local environment

Sven Heiles, Richard J. Cooper, Matthew J. DiTucci and Evan R. Williams*

Infrared spectroscopy of guanidinium confined in gaseous nanodrops shows hydration depends on local environment and lends new insights into its effectiveness as a protein denaturant.

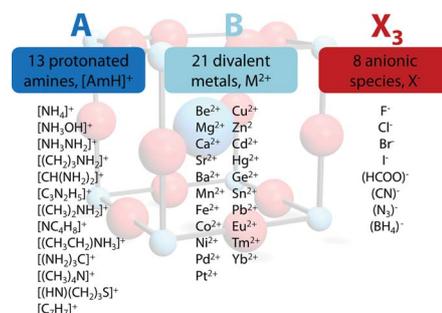


3430

An extended Tolerance Factor approach for organic–inorganic perovskites

Gregor Kieslich,* Shijing Sun and Anthony K. Cheetham*

Tolerance Factors of possible hybrid perovskites are calculated for over 2500 amine-metal-anion permutations of the periodic table.

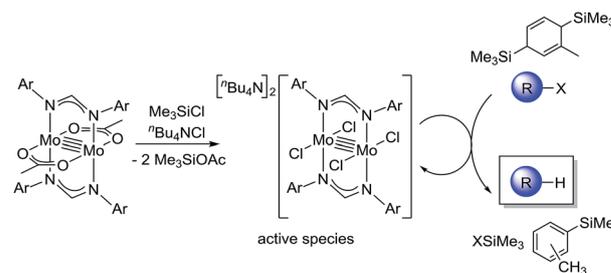


3434

Mixed-ligand complexes of paddlewheel dinuclear molybdenum as hydrodehalogenation catalysts for polyhaloalkanes

Hayato Tsurugi,* Akio Hayakawa, Shun Kando, Yoshitaka Sugino and Kazushi Mashima*

A mixed-ligated dimolybdenum complex Mo₂(OAc)₂[CH(NAr)₂]₂ in combination with 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene and ⁿBu₄NCl exhibited high catalytic activity for hydrodehalogenation reactions.

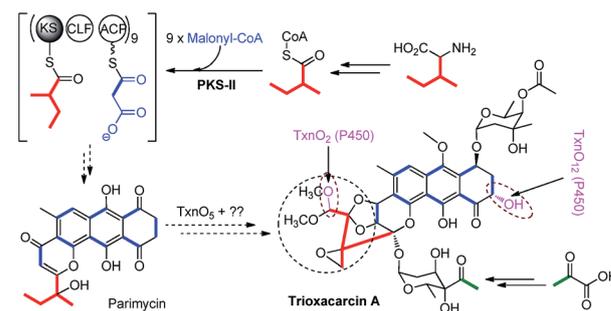


3440

Biosynthesis of trioxacarcin revealing a different starter unit and complex tailoring steps for type II polyketide synthase

Mei Zhang, Xian-Feng Hou, Li-Hua Qi, Yue Yin, Qing Li, Hai-Xue Pan, Xin-Ya Chen and Gong-Li Tang*

Different starter unit and complex tailoring steps for type II polyketide synthase in trioxacarcin biosynthesis.



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**Accessible Products**

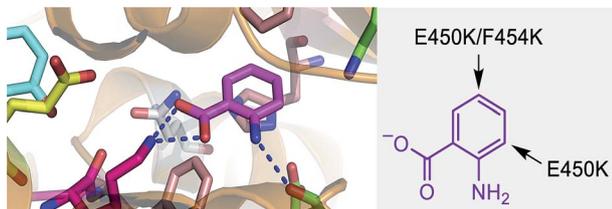
Glycoside Stereochemistry	β-manno	Glycoside Functionality	2-benzyloxy
	α-gluco		2-acyloxy
	β-gluco		2-deoxy
			2-azido

Sugar silanes: versatile reagents for stereocontrolled glycosylation via intramolecular aglycone delivery

Jordan T. Walk, Zachary A. Buchan
and John Montgomery*

A new method for the intramolecular glycosylation of alcohols is described.

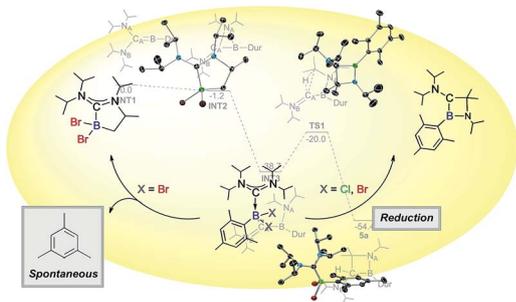
3454

**Extending the biocatalytic scope of regiocomplementary flavin-dependent halogenase enzymes**

Sarah A. Shepherd, Chinnan Karthikeyan,
Jonathan Latham, Anna-Winona Struck, Mark
L. Thompson, Binuraj R. K. Menon, Matthew Q. Styles,
Colin Levy, David Leys and Jason Micklefield*

Targeted mutagenesis increases the activity and alters the regioselectivity of flavin-dependent halogenases.

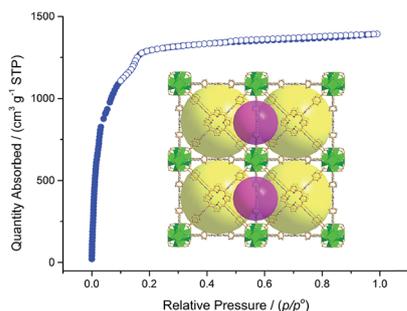
3461

**Generation of 1,2-azaboretidines via reduction of ADC borane adducts**

H. Braunschweig,* A. Gackstatter, T. Kupfer, T. Scheller,
F. Hupp, A. Damme, N. Arnold and W. C. Ewing

ADC borane adducts $\text{RBX}_2 \cdot \text{ADC}$ (R = Mes, Dur; X = Cl, Br; ADC = $:\text{C}(\text{NiPr}_2)_2$) have been prepared and reduced by KC_8 to afford air stable 1,2-azaboretidines with high selectivity.

3466

**Stable porphyrin Zr and Hf metal–organic frameworks featuring 2.5 nm cages: high surface areas, SCSC transformations and catalyses**

Jun Zheng, Mingyan Wu,* Feilong Jiang, Weiping Su*
and Maochun Hong

Two isostructural porphyrin Zr and Hf metal–organic frameworks (FJI-H6 and FJI-H7) are rationally synthesized, and are constructed from 2.5 nm cubic cages.

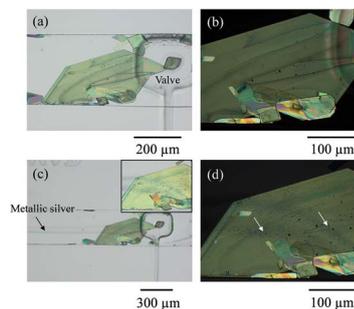


3471

Bottom-up on-crystal in-chip formation of a conducting salt and a view of its restructuring: from organic insulator to conducting "switch" through microfluidic manipulation

Josep Puigmartí-Luis,^{*} Markos Paradinas, Elena Bailo, Romen Rodríguez-Trujillo, Raphael Pfattner, Carmen Ocal^{*} and David B. Amabilino^{*}

The chemical modification of an immobilized single crystal in a fluid cell is reported, whereby a material with switching functions is generated with reagent in the stream.

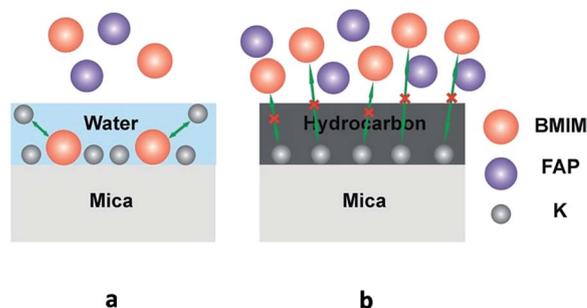


3478

What causes extended layering of ionic liquids on the mica surface?

Xiao Gong, Andrew Kozbial and Lei Li^{*}

The adsorbed water on the mica surface is the key to the extended layering of ILs.

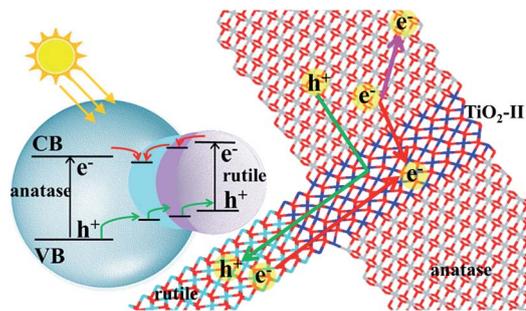


3483

Three-phase junction for modulating electron–hole migration in anatase–rutile photocatalysts

Wei-Na Zhao, Sheng-Cai Zhu, Ye-Fei Li and Zhi-Pan Liu^{*}

Theory resolves the anatase–rutile phase junction structure and characterizes its role in photocatalysis as a *single-way valve* modulating electron–hole separation.

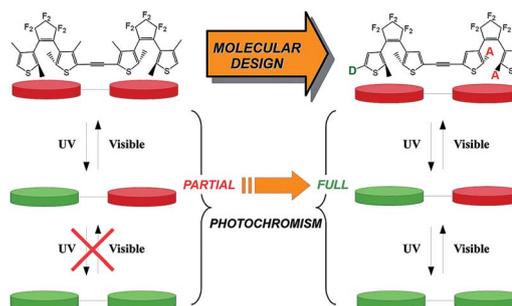


3495

Designing efficient photochromic dithienylethene dyads

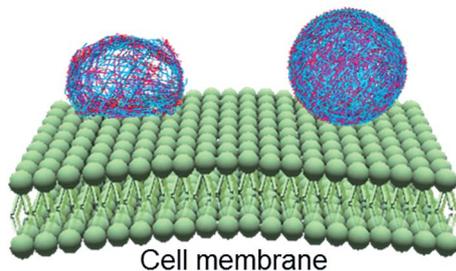
Arnaud Fihey and Denis Jacquemin^{*}

The impact of chemical substitution on the optical properties of *ca.* 30 dithienylethene (DTE) dyads is investigated with first-principles approaches, with the aim to provide useful guidelines for obtaining more efficient DTE multimers.



3505

Soft HA capsules Stiff HA capsules

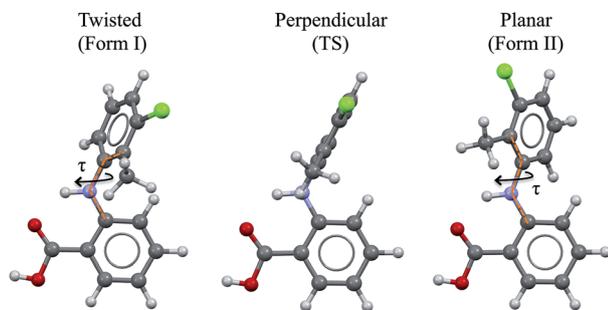


The role of capsule stiffness on cellular processing

Huanli Sun, Edgar H. H. Wong, Yan Yan, Jiwei Cui, Qiong Dai, Junling Guo, Greg G. Qiao* and Frank Caruso*

A systematic and quantitative study on the role of capsule stiffness in cellular processing was performed using hyaluronic acid capsules with tunable stiffness constructed *via* continuous assembly of polymers.

3515

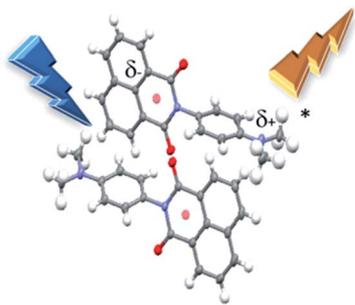


Can the study of self-assembly in solution lead to a good model for the nucleation pathway? The case of tolfenamic acid.

W. Du, A. J. Cruz-Cabeza, S. Woutersen, R. J. Davey* and Q. Yin

To further our understanding of the role of solution chemistry in directing nucleation processes new experimental and computational data are presented on the solution and crystallisation chemistry of tolfenamic acid (TA), a benchmark polymorphic compound.

3525

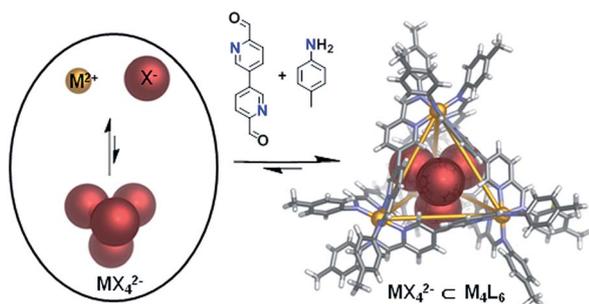


Polymorph crystal packing effects on charge transfer emission in the solid state

Xiaoyan He, Andrew C. Benniston,* Hanna Saarenpää, Helge Lemmetyinen, Nikolia V. Tkachenko* and Ulrich Baisch

Condensation of 1,8-naphthalic anhydride with *N,N*-(dimethylamino)aniline produced the donor-acceptor compound **DMIM**, which crystallised from a chloroform–diethyl ether mixture to afford two different coloured crystal polymorphs.

3533



Mutual stabilisation between $M^II_4L_6$ tetrahedra and $M^II X_4^{2-}$ metallate guests

Imogen A. Riddell, Tanya K. Ronson and Jonathan R. Nitschke*

A series of $[M^II X_4]^{2-} \subset M^II_4 L_6$ host–guest complexes are formed through the mutual stabilisation of the host and guest complexes; neither the host nor guest is stable in the absence of the other.

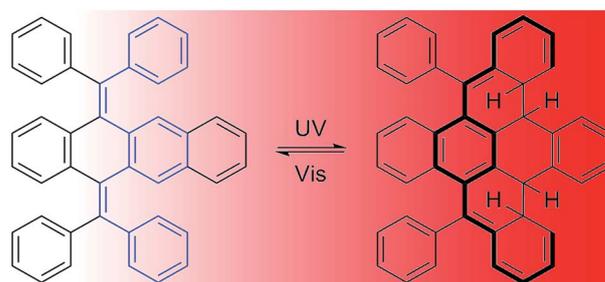


3538

Aggregation-induced emission and aggregation-promoted photochromism of bis(diphenylmethylene)dihydroacenes

Zikai He, Liang Shan, Ju Mei, Hong Wang, Jacky W. Y. Lam, Herman H. Y. Sung, Ian D. Williams, Xiao Gu, Qian Miao* and Ben Zhong Tang*

Solid-state photochromism was found in bis(diphenylmethylene)dihydroacenes, caused by photocyclization of the embedded *cis*-stilbene motifs.

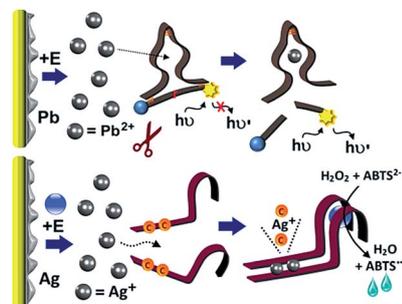


3544

Addressing, amplifying and switching DNAzyme functions by electrochemically-triggered release of metal ions

Lina Freage, Alexander Trifonov, Ran Tel-Vered, Eyal Golub, Fuan Wang, John S. McCaskill and Itamar Willner*

The addressable potential-controlled release of metal ions into electrolyte solutions containing mixtures of nucleic acids leads to the metal ion-guided generation of different DNAzymes and to the activation of DNA cascades.

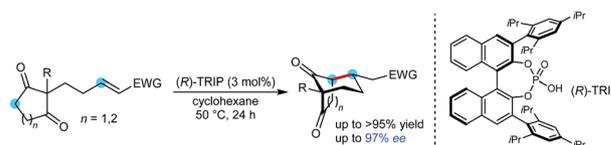


3550

Enantioselective synthesis of bicyclo[3.n.1]alkanes by chiral phosphoric acid-catalyzed desymmetrizing Michael cyclizations

Alan R. Burns, Amaël G. E. Madec, Darryl W. Low, Iain D. Roy and Hon Wai Lam*

2,2-Disubstituted cyclic 1,3-diketones containing a tethered electron-deficient alkene undergo chiral phosphoric acid-catalyzed desymmetrizing Michael cyclizations to give bridged bicyclic products in high enantioselectivities.

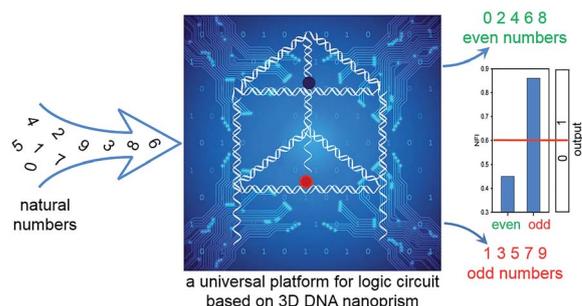


3556

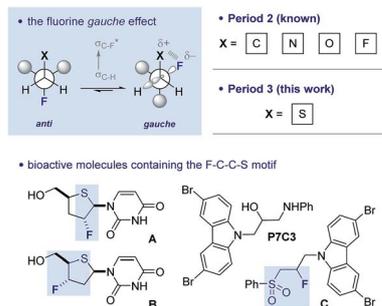
A universal platform for building molecular logic circuits based on a reconfigurable three-dimensional DNA nanostructure

Kaiyu He, Yong Li, Binbin Xiang, Peng Zhao, Yufang Hu, Yan Huang, Wang Li, Zhou Nie* and Shouzhao Yao

Integrating multiple components of a logic device into a 3D DNA nanoprism provides a universal platform for constructing diverse logic gates.



3565

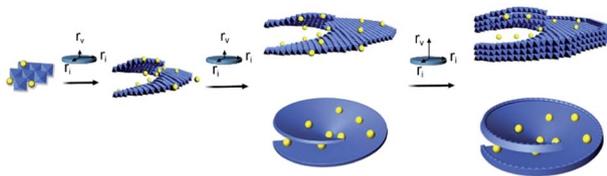


Can acyclic conformational control be achieved via a sulfur–fluorine *gauche* effect?

C. Thiehoff, M. C. Holland, C. Daniliuc, K. N. Houk* and R. Gilmour*

Herein detailed conformational analyses of β -fluorosulfides, -sulfoxides and -sulfones are disclosed, thus extending the scope of the fluorine *gauche* effect to the 3rd Period (X = SR, SOR, SO₂R; $\phi_{\text{FCCS}} \approx 60^\circ$).

3572

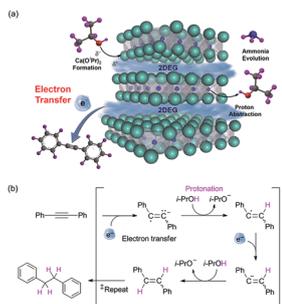


Edge overgrowth of spiral bimetallic hydroxides ultrathin-nanosheets for water oxidation

Bing Ni and Xun Wang*

We have synthesized spiral ultrathin-nanosheets with overgrown edges of NiFe, CoNi and CoFe bimetallic hydroxides which show excellent performance for the OER.

3577

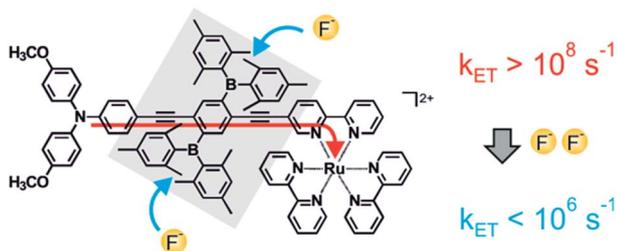


Two dimensional inorganic electride-promoted electron transfer efficiency in transfer hydrogenation of alkynes and alkenes

Ye Ji Kim, Sun Min Kim, Eun Jin Cho, Hideo Hosono, Jung Woon Yang* and Sung Wng Kim*

A simple and highly efficient transfer hydrogenation of alkynes and alkenes by using a two-dimensional electride, dicalcium nitride ($[\text{Ca}_2\text{N}]^+ \cdot \text{e}^-$), as an electron transfer agent is disclosed.

3582



Fluoride binding to an organoboron wire controls photoinduced electron transfer

Jing Chen and Oliver S. Wenger*

The efficiency of organoboron wires as mediators of long-range electron transfer can be controlled by anion binding.

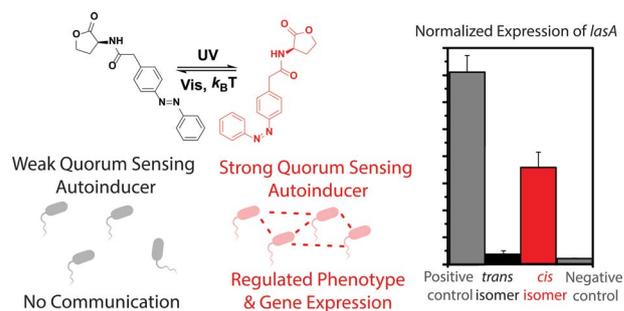


3593

Controlling the activity of quorum sensing autoinducers with light

J. P. Van der Berg, W. A. Velema, W. Szymanski, A. J. M. Driessen* and B. L. Feringa*

Bacteria use Quorum Sensing (QS) to organize into communities and synchronize gene expression. Here we report on a method to externally interfere with QS system using light.

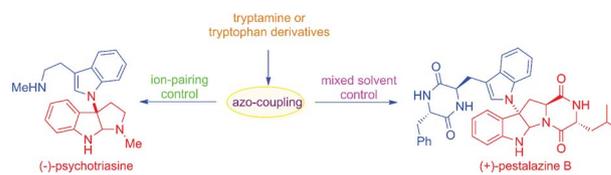


3599

Enantioselective and diastereoselective azo-coupling/iminium-cyclizations: a unified strategy for the total syntheses of (–)-psychotriasine and (+)-pestalazine B

Qi Li, Tingting Xia, Licheng Yao, Haiteng Deng* and Xuebin Liao*

We report a unified strategy for the total syntheses of (–)-psychotriasine and (+)-pestalazine B based on the advanced intermediates of 3 α -amino-hexahydropyrrolo-[2,3-*b*]indole.

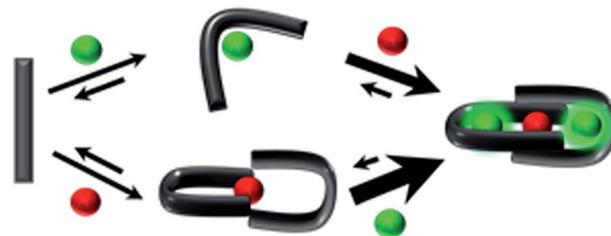


3606

A prochelator peptide designed to use heterometallic cooperativity to enhance metal ion affinity

Bruno Alies, Jacob D. Wiener and Katherine J. Franz*

A peptide has been designed so that its chelating affinity for one type of metal ion regulates its affinity for a second, different type of metal ion.

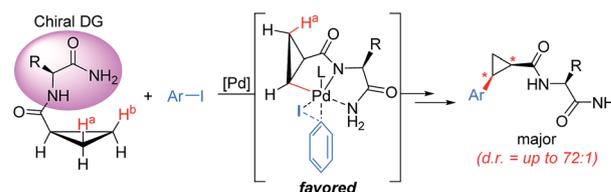


3611

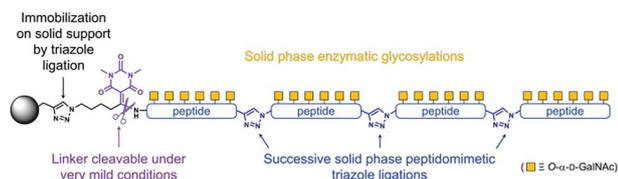
Asymmetric C–H functionalization of cyclopropanes using an isoleucine-NH₂ bidentate directing group

Jinhee Kim, Mikyung Sim, Namhoon Kim and Sungwoo Hong*

The use of an Ile-NH₂ auxiliary can provide excellent levels of asymmetric induction in the Pd(II)-catalyzed C(sp³)-H functionalization of cyclopropanes.



3617

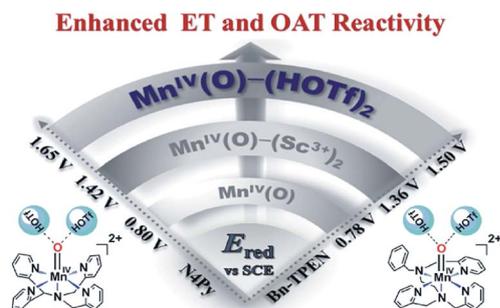


Combining triazole ligation and enzymatic glycosylation on solid phase simplifies the synthesis of very long glycoprotein analogues

Mathieu Galibert, Véronique Piller, Friedrich Piller, Vincent Aucagne* and Agnès F. Delmas

Solid phase chemical ligation followed by enzymatic glycosylation exploits the advantages of a solid support to minimize the purification steps, constituting a promising approach for the synthesis of complex glycoproteins.

3624



Tuning the reactivity of mononuclear nonheme manganese(IV)-oxo complexes by triflic acid

Junying Chen, Heejung Yoon, Yong-Min Lee, Mi Sook Seo, Ritimukta Sarangi, Shunichi Fukuzumi* and Wonwoo Nam*

Binding of two HOTf molecules to $Mn^{IV}(O)$ species resulted in contrasting effects on the reactivities in oxygen atom transfer and H-atom transfer reactions.

CORRECTION

3633

Correction: Cobalt co-catalysis for cross-electrophile coupling: diarylmethanes from benzyl mesylates and aryl halides

Laura K. G. Ackerman, Lukiana L. Anka-Lufford, Marina Naodovic and Daniel J. Weix*

RETRACTION

3634

Retraction: Homonuclear bond activation using a stable *N,N'*-diamidocarbene

Kelly M. Wiggins, Jonathan P. Moerdyk and Christopher W. Bielawski*

