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PERSPECTIVES

3663

Self-assembly of "patchy" nanoparticles: a versatile approach to functional hierarchical materials

David J. Lunn, John R. Finnegan and Ian Manners*

The solution-phase self-assembly or "polymerization" of discrete colloidal building blocks, such as "patchy" nanoparticles and multicompartment micelles, is attracting growing attention with respect to the creation of complex hierarchical materials.

3674

Chemical principles underpinning the performance of the metal-organic framework HKUST-1

Christopher H. Hendon and Aron Walsh*

HKUST-1 has emerged as the bastion of multifunctional hybrid solids; we discuss the past, present and future of Cu-based metal–organic frameworks.





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Porous ionic liquids: synthesis and application

Shiguo Zhang, Kaoru Dokko and Masayoshi Watanabe*

Porous ionic liquids combine the unique characteristics of ionic liquids with the common features of polymers and porous materials.



EDGE ARTICLES

3692

A general approach to the design of allosteric, transcription factor-regulated DNAzymes

G. Adornetto, A. Porchetta, G. Palleschi, K. W. Plaxco and F. Ricci*

Here we explore a general strategy for the rational design of nucleic acid catalysts that can be allosterically activated by specific nucleic-acid binding proteins.



3697

Exceptional CO₂ working capacity in a heterodiamine-grafted metal-organic framework

Woo Ram Lee, Hyuna Jo, Li-Ming Yang, Hanyeong Lee, Dae Won Ryu, Kwang Soo Lim, Jeong Hwa Song, Da Young Min, Sang Soo Han, Jeong Gil Seo, Yong Ki Park, Dohyun Moon and Chang Seop Hong^{*}

The amine functionalized material **1-dmen** shows a record high working capacity for CO_2 capture at low regeneration temperatures compared with other MOFs. Furthermore, this performance is maintained upon exposure to humidity.

3706

Carbene catalyzed umpolung of α , β -enals: a reactivity study of diamino dienols *vs.* azolium enolates, and the characterization of advanced reaction intermediates

Veera Reddy Yatham, Jörg-M. Neudörfl, Nils E. Schlörer and Albrecht Berkessel*

NMR/X-ray evidence is provided for hitherto postulated reactivity patterns of homoenolate *vs.* azolium enolate intermediates in NHC-catalyzed umpolung of enals.





EDGE ARTICLES

3712 Modulated protein function Directed assembly on graphene ISI 3718



Visible lightby different

ISC

3724 Supramolecular Triplet Photosensitize Implementation ISC harvesting and chromophores; Easily interchangeable H-bonding modules Intra-assembly Singlet/Triplet ping-pong Energy Transfer $\tau_{\rm T} = 263$

3738



Functional modulation and directed assembly of an enzyme through designed non-natural post-translation modification

Andrew M. Hartley, Athraa J. Zaki, Adam R. McGarrity, Cecile Robert-Ansart, Andriy V. Moskalenko, Gareth F. Jones, Monica F. Craciun, Saverio Russo, Martin Elliott, J. Emyr Macdonald and D. Dafydd Jones*

Designed phenyl azide incorporation combined with bioorthogonal Click chemistry to regulate enzyme activity, or promote its stable assembly on graphene.

Enantioselective installation of adjacent tertiary benzylic stereocentres using lithiation-borylationprotodeboronation methodology. Application to the synthesis of bifluranol and fluorohexestrol

Stefan Roesner, Daniel J. Blair and Varinder K. Aggarwal*

Highly hindered benzylic carbamates have been reacted with hindered boronic esters to give tertiary boronic esters with very high diastereo- and enantiocontrol and the methodology has been applied to otherwise difficult-toaccess molecules.

Bodipy-C₆₀ triple hydrogen bonding assemblies as heavy atom-free triplet photosensitizers: preparation and study of the singlet/triplet energy transfer

Song Guo, Liang Xu, Kejing Xu, Jianzhang Zhao,* Betül Küçüköz, Ahmet Karatay, Halime Gul Yaglioglu, Mustafa Hayvali and Ayhan Elmali

Hydrogen bonding-mediated supramolecular triplet photosensitizers with easily interchangeable visible lightharvesting Bodipy modules and the fullerene intersystem crossing module were devised.

Soft hydrogen bonds to alkenes: the methanol-ethene prototype under experimental and theoretical scrutiny

Matthias Heger, Ricardo A. Mata and Martin A. Suhm*

Theory meets experiment for the simplest model of alcohol-alkene hydrogen bonding and both support a close to harmonic description.

Counterion influence on the N-I-N halogen bond

Michele Bedin, Alavi Karim, Marcus Reitti, Anna-Carin C. Carlsson, Filip Topić, Mario Cetina, Fangfang Pan, Vaclav Havel, Fatima Al-Ameri, Vladimir Sindelar, Kari Rissanen, Jürgen Gräfenstein and Máté Erdélyi*

Counterions influence three-center halogen bonds differently than coordination bonds of transition metals.

3757

Chemical speciation of MeHg⁺ and Hg²⁺ in aqueous solution and HEK cells nuclei by means of DNA interacting fluorogenic probes

B. Díaz de Greñu, J. García-Calvo, J. V. Cuevas, G. García-Herbosa, B. García, N. Busto, S. Ibeas, T. Torroba,* B. Torroba, A. Herrera and S. Pons*

Speciation of Hg²⁺ and MeHg⁺ has been achieved by *in vitro* approaches with fluorogenic probes supported in cultured cells.

3765

Absolute structure determination of compounds with axial and planar chirality using the crystalline sponge method

Shota Yoshioka, Yasuhide Inokuma, Manabu Hoshino, Takashi Sato and Makoto Fujita*

The absolute structure determination of compounds with axial and planar chirality obtained by recently developed asymmetric syntheses was achieved using the crystalline sponge method without using any reference compounds or synthetic modifications.

3769

Micro-competition system for Raman quantification of multiple glycans on intact cell surface

Yunlong Chen, Lin Ding, Junqiang Xu, Wanyao Song, Min Yang, Junjie Hu and Huangxian Ju*

A micro-competition system integrated functionalized silica bubbles and Raman encoded nanoprobes to simultaneously assay multiple glycans on intact cell surfaces.















Supramolecularly engineered phospholipids constructed by nucleobase molecular recognition: upgraded generation of phospholipids for drug deliverv

Dali Wang, Chunlai Tu, Yue Su, Chuan Zhang, Udo Greiser, Xinyuan Zhu,* Deyue Yan and Wenxin Wang*

Supramolecularly engineered phospholipids and liposomes based on complementary hydrogen bonding of nucleosides have been developed.

Systematic re-evaluation of the bis(2-hydroxyethyl)disulfide (HEDS) assay reveals an alternative mechanism and activity of glutaredoxins

Patricia Begas, Verena Staudacher and Marcel Deponte^{*}

The sequential kinetic patterns of mono- and dithiol glutaredoxins in the HEDS assay reflect an alternative enzymatic mechanism for the glutathione-dependent reduction of disulfide substrates.





3805

Highly efficient near ultraviolet organic light-emitting diode based on a meta-linked donor-acceptor molecule

Haichao Liu, Qing Bai, Liang Yao, Haiyan Zhang, Hai Xu, Shitong Zhang, Weijun Li, Yu Gao, Jinyu Li, Ping Lu, Hongyan Wang, Bing Yang* and Yuguang Ma

A meta-linked donor-acceptor (D-A) structure was utilized to achieve high-efficiency and colour-purity near ultraviolet (NUV) in organic light-emitting diodes (OLEDs).



Ammonia decomposition catalysis using non-stoichiometric lithium imide

Joshua W. Makepeace, Thomas J. Wood, Hazel M. A. Hunter, Martin O. Jones and William I. F. David*

The non-stoichiometric lithium imide-amide system effectively decomposes ammonia to its constituents, hydrogen and nitrogen. Isotopic studies show that this bulk catalytic reaction has the potential to generate high-purity hydrogen for future energy and transport applications.

Holo CvlH

KS AT ACP T

śн

3816

Assembly line termination in cylindrocyclophane biosynthesis: discovery of an editing type II thioesterase domain in a type I polyketide synthase

H. Nakamura, J. X. Wang and E. P. Balskus*

Investigation of cylindrocyclophane biosynthesis reveals a C-terminal thioesterase domain involved in PKS assembly line editing, not termination.

3823

Luminescent platinum(II) complexes with self-assembly and anti-cancer properties: hydrogel, pH dependent emission color and sustained-release properties under physiological conditions

Johnson Lui-Lui Tsai, Taotao Zou, Jia Liu, Tianfeng Chen, Anna On-Yee Chan, Chen Yang, Chun-Nam Lok and Chi-Ming Che^{*}

Luminescent platinum(II) complexes show anti-cancer and pH-dependent self-assembly and sustained-release properties under physiological conditions.

3831

Cytotoxicity of guanine-based degradation products contributes to the antiproliferative activity of guanine-rich oligonucleotides

Nan Zhang, Tao Bing, Xiangjun Liu, Cui Qi, Luyao Shen, Linlin Wang and Dihua Shangguan*

Guanine-rich oligonucleotides with lower nuclease resistance exhibited higher antiproliferative activity; guanine-based compounds showed highly concentrationdependent cytotoxicity.

3839

A two-dimensional molecular beacon for mRNA-activated intelligent cancer theranostics

Dan Wu, Guofen Song, Zhi Li, Tao Zhang, Wei Wei, Muzi Chen, Xuewen He and Nan Ma^{*}

A two-dimensional quantum dot molecular beacon with interconnected imaging and therapy modalities is developed for intelligent cancer theranostics.



Stalled CvIH

AT ACP

Me

Cylindrocyclophanes A-I

CVIH TE

A role in assembly line editing, not termination









Insights on spin polarization through the spin density source function

Carlo Gatti,* Ahmed M. Orlando and Leonardo Lo Presti

The source function for the spin density $s(\mathbf{r})$ is introduced, allowing the H and O influence on $s(\mathbf{r})$ to be disentangled.

Dual wavelength asymmetric photochemical synthesis with circularly polarized light

R. D. Richardson, M. G. J. Baud, C. E. Weston, H. S. Rzepa, M. K. Kuimova^{*} and M. J. Fuchter^{*}

An asymmetric photchemical synthesis of a dihyrohelicene demonstrates two wavelengths of circularly polarized (CP) light can be used to ensure the enantiomeric induction intrinsic to each step can combine additively; significantly increasing the asymmetric induction possible over a single wavelength approach.

3863



Tailoring of the desired selectivity and the turn-on detection range in a self-assembly-based fluorescence sensory system

Takao Noguchi,* Bappaditya Roy, Daisuke Yoshihara, Youichi Tsuchiya, Tatsuhiro Yamamoto and Seiji Shinkai*

A new assembly-based fluorescent sensor exhibits much improved selectivity for ATP over ADP and a broad detection range under adjusted salt conditions, providing insight into a pivotal binding mechanism in the self-assembly process.

3868



4.4 nm nanoparticles composed of >1400 atoms

How to determine accurate chemical ordering in several nanometer large bimetallic crystallites from electronic structure calculations

Sergey M. Kozlov, Gábor Kovács, Riccardo Ferrando and Konstantin M. Neyman*

The proposed method allows to efficiently determine the atomic arrangement in bimetallic nanoparticles based on electronic structure calculations and unravels the relationship between structural preferences of atoms and binding in nanoalloys.

Significant improvement of oxidase activity through the genetic incorporation of a redox-active unnatural amino acid

Yang Yu, Qing Zhou, Li Wang, Xiaohong Liu, Wei Zhang, Meirong Hu, Jianshu Dong, Jiasong Li, Xiaoxuan Lv, Hanlin Ouyang, Han Li, Feng Gao, Weimin Gong, Yi Lu* and Jiangyun Wang*

Incorporation of 3-methoxytyrosine boosts the oxidase activity of the myoglobin model of oxidase, stressing the importance of the redox potential tuning of tyrosine.

3886

Unified total synthesis of the natural products endiandric acid A, kingianic acid E, and kingianins A, D, and F

S. L. Drew, A. L. Lawrence* and M. S. Sherburn*

A measure of the strength of a synthetic strategy is its versatility: specifically, whether it allows structurally distinct targets to be prepared. This work describes the total synthesis of natural products of three distinct structural types from a common intermediate.

3891

Thorium–ligand multiple bonds *via* reductive deprotection of a trityl group

Danil E. Smiles, Guang Wu, Nikolas Kaltsoyannis* and Trevor W. Hayton*

Reductive deprotection of the trityl group from $[Th(ECPh_3)(NR_2)_3]$ (E = O, S), by reaction with KC₈, in the presence of 18-crown-6, affords the thorium oxo complex, $[K(18-crown-6)][Th(O)(NR_2)_3]$, and the thorium sulphide complex, $[K(18-crown-6)][Th(S)(NR_2)_3]$, respectively.

3900

Multiscale electrochemistry of hydrogels embedding conductive nanotubes

Jean-Marc Noël, Léopold Mottet, Nicolas Bremond, Philippe Poulin, Catherine Combellas, Jérôme Bibette and Frédéric Kanoufi*

The local functionalities of biocompatible objects can be characterized under conditions similar to the operating ones, using scanning electrochemical microscopy (SECM).









(cc) BY

3915

Ni:Pt

90:10

70.30

Fragmentation

ores of the right

dimensior

Pores too small



Multiplexed detection of serological cancer markers with plasmon-enhanced Raman spectro-immunoassay

Ming Li,* Jeon Woong Kang, Saraswati Sukumar, Ramachandra Rao Dasari and Ishan Barman*

A plasmon-enhanced Raman spectroscopic assay has been developed for multiplexed detection of breast cancer markers—with high sensitivity and exquisite specificity, offering the potential of evaluating the breast cancer burden accurately.

The atomistic origin of the extraordinary oxygen reduction activity of Pt_3Ni_7 fuel cell catalysts

Alessandro Fortunelli,* William A. Goddard III,* Luca Sementa, Giovanni Barcaro, Fabio R. Negreiros and Andrés Jaramillo-Botero

Optimality of Pt : Ni 30 : 70 fully dealloyed nanoporous Pt particles in terms of size and coordination environment.



A single crystalline porphyrinic titanium metal-organic framework

Shuai Yuan, Tian-Fu Liu, Dawei Feng, Jian Tian, Kecheng Wang, Junsheng Qin, Qiang Zhang, Ying-Pin Chen, Mathieu Bosch, Lanfang Zou, Simon J. Teat, Scott J. Dalgarno and Hong-Cai Zhou^{*}

We have successfully synthesized a single crystalline porphyrinic titanium MOF, namely PCN-22. PCN-22 represents an important step towards mimicking dye sensitized TiO₂ in MOFs.

3931



Chemical sensing in two dimensional porous covalent organic nanosheets

Gobinda Das, Bishnu P. Biswal, Sharath Kandambeth, V. Venkatesh, Gagandeep Kaur, Matthew Addicoat, Thomas Heine, Sandeep Verma and Rahul Banerjee*

Covalent organic nanosheets (CONs) were synthesised from imide functionalised COFs. **TfpBDH**-CONs exhibit a "turn-on" detection capability for 2,4,6-trinitrophenol in the solid state, but show a "turn-off" detection in the dispersion state.

Nitrogen fixation catalyzed by ferrocene-substituted dinitrogen-bridged dimolybdenum-dinitrogen complexes: unique behavior of ferrocene moiety as redox active site

Shogo Kuriyama, Kazuya Arashiba, Kazunari Nakajima, Hiromasa Tanaka, Kazunari Yoshizawa* and Yoshiaki Nishibayashi*

Mo–N₂ complex bearing ferrocenes as redox-active units efficiently catalyses the formation of ammonia from molecular dinitrogen under ambient conditions.

3952

Tissue distribution and urinary excretion of intravenously administered chemically functionalized graphene oxide sheets

Dhifaf A. Jasim, Cécilia Ménard-Moyon, Dominique Bégin, Alberto Bianco^{*} and Kostas Kostarelos^{*}

Providing a pharmacological understanding on how chemically functionalized GO sheets transport in the blood stream and interact with physiological barriers that determine their body excretion and tissue accumulation.

3965

Chemical looping of metal nitride catalysts: low-pressure ammonia synthesis for energy storage

R. Michalsky,* A. M. Avram, B. A. Peterson, P. H. Pfromm and A. A. Peterson

Design principles for reducible metal nitride catalysts are developed and demonstrated for ambient-pressure solar-driven N_2 reduction into $\rm NH_3.$

3975

Supramolecular free radicals: near-infrared organic materials with enhanced photothermal conversion

Yang Jiao, Kai Liu, Guangtong Wang, Yapei Wang and Xi Zhang*

A novel kind of supramolecular free radical with significantly improved free radical yield and enhanced near-infrared photothermal conversion has been fabricated.













Investigating pyridazine and phthalazine exchange in a series of iridium complexes in order to define their role in the catalytic transfer of magnetisation from *para*-hydrogen

Kate M. Appleby, Ryan E. Mewis, Alexandra M. Olaru, Gary G. R. Green, Ian J. S. Fairlamb and Simon B. Duckett*

Reaction of [Ir(IMes)(COD)Cl] with pyridazine (pdz) or phthalazine (phth) and H₂ results in the formation of the *para*-hydrogen magnetisation transfer catalysts [Ir(H)₂(IMes)(pdz)₃]Cl and [Ir(H)₂(IMes)(phth)₃]Cl.

Cobalt-catalysed asymmetric hydrovinylation of 1,3-dienes

Yam N. Timsina, Rakesh K. Sharma and T. V. RajanBabu*

Excellent selectivity with complexes of DIOP, BDPP and Josiphos with E-1,3-dienes reacting faster than the Z-isomers at low temperatures.

4009

3994

Ŕ

ethylene (1 atm.)

[P~P]CoCl₂, MAO (cat.)

CH₂Cl₂ - 45 °C to rt

R = alkyl, CH₂CO₂Et, CH₂OBn



(90% yield

90-99% ee)

[(S,S)-BDPP]CoCl₂

Oxygen deficient α -Fe₂O₃ photoelectrodes: a balance between enhanced electrical properties and trap-mediated losses

Mark Forster, Richard J. Potter, Yichuan Ling, Yi Yang, David R. Klug, Yat Li and Alexander J. Cowan*

Intrinsic doping of hematite through the inclusion of oxygen vacancies (V_O) is being increasingly explored as a simple, low temperature route to preparing active water splitting α -Fe₂O_{3-x} photoelectrodes.

4017



Cyclo-oligomerization of isocyanates with Na(PH₂) or Na(OCP) as " P^{-1} " anion sources

Dominikus Heift, Zoltán Benkő,* Hansjörg Grützmacher,* Andrew R. Jupp and Jose M. Goicoechea

Na(OCP) initiates the catalytic cyclo-trimerization of isocyanates involving the mutual formation of P-heterocycles and spiro phosphoranides (shown on the right) as reactive intermediates.

pH-Controlled selection between one of three guests from a mixture using a coordination cage host

William Cullen, Katie A. Thomas, Christopher A. Hunter^{*} and Michael D. Ward^{*}

We demonstrate the use of a simple pH swing to control the selection of one of three different guests from aqueous solution by a coordination cage host.



Sub-5 nm porous nanocrystals: interfacial sitedirected growth on graphene for efficient biocatalysis

Biao Kong, Xiaotian Sun, Cordelia Selomulya, Jing Tang, Gengfeng Zheng, Yingqing Wang* and Dongyuan Zhao*

An interfacial site-directed, capping-agent-free growth method for direct production of macromolecular scale (sub-5 nm) porous nanocrystals that are fully crystalline with a high surface area were developed for efficient biocatalysis.

4035

Steric shielding vs. $\sigma-\pi$ orbital interactions in triplet-triplet energy transfer

Inmaculada Andreu, Isabel Morera, Fabrizio Palumbo, German Sastre, Francisco Bosca* and Miguel A. Miranda*

Fine tuning of the benzoylthiophene triplet level through $\sigma - \pi$ orbital interactions modifies the energy transfer rate constants to appropriate acceptors.

4042

Development of peptoid-based ligands for the removal of cadmium from biological media

Abigail S. Knight, Effie Y. Zhou and Matthew B. Francis*

To address the lack of current therapeutic strategies for cadmium poisoning, peptoid-based ligands are identified using combinatorial chemistry that can selectively coordinate cadmium in a complex biological sample matrix.













Mesoporous 2D covalent organic frameworks based on shape-persistent arylene-ethynylene macrocycles

Haishen Yang, Ya Du, Shun Wan, George Devon Trahan, Yinghua Jin and Wei Zhang^{*}

Covalent organic frameworks with high porosity and crystallinity have been synthesized, through macrocycle-toframework strategy, using shape-persistent arylene-ethynylene macrocycles as the key components to control the topology and modulate the porosity.

Post-synthetic halide conversion and selective halogen capture in hybrid perovskites

D. Solis-Ibarra, I. C. Smith and H. I. Karunadasa*

Halides in 3D perovskites can be exchanged using halogen gas, while 2D perovskites can be tuned for selective halogen chemisorption.

4060



Enzyme repurposing of a hydrolase as an emergent peroxidase upon metal binding

Nobutaka Fujieda,* Jonas Schätti, Edward Stuttfeld, Kei Ohkubo, Timm Maier, Shunichi Fukuzumi and Thomas R. Ward*

Adding a metal cofactor to a protein bearing a latent metal binding site endows the macromolecule with nascent catalytic activity.

4066



Doping-induced memory effect in Li-ion batteries: the case of Al-doped $Li_4Ti_5O_{12}$

De Li, Yang Sun, Xizheng Liu, Ruwen Peng and Haoshen Zhou*

A memory effect in Li-ion batteries can be induced and tailored by element doping, such as Al-doping in spinel $Li_4Ti_5O_{12}$.

Solution structural characterization of an array of nanoscale aqueous inorganic $Ga_{13-x}In_x$ ($0 \le x \le 6$) clusters by ¹H-NMR and QM computations

Anna F. Oliveri, Lindsay A. Wills, Caitlyn R. Hazlett, Matthew E. Carnes, I-Ya Chang, Paul Ha-Yeon Cheong* and Darren W. Johnson*

Complete structural determination by ¹H NMR spectroscopy and QM computations reveals a series of heterometallic Ga_{13-x}In_x(µ₃-OH)₆(µ₂-OH)₁₈(H₂O)₂₄](NO₃)₁₅ clusters persist in solution and can exist as an isomeric mixture.

4086

III-defined concepts in chemistry: rigid force constants *vs.* compliance constants as bond strength descriptors for the triple bond in diboryne

Jörg Grunenberg*

In a recent publication in this journal, the interpretation of the Braunschweig's diboryne as a true triple bond is questioned.





4089

The boron-boron triple bond in $NHC \rightarrow B \equiv B \leftarrow NHC$

Nicole Holzmann, Markus Hermann and Gernot Frenking*

Thorough examination of the electronic structure of the compound $B_2(NHC^{Me})_2$ provides convincing evidence for a $B \equiv B$ triple bond.



4095

Versatile rare earth hexanuclear clusters for the design and synthesis of highly-connected ftw-MOFs

Ryan Luebke, Youssef Belmabkhout, Łukasz J. Weseliński, Amy J. Cairns, Mohamed Alkordi, George Norton, Łukasz Wojtas, Karim Adil and Mohamed Eddaoudi*

A targeted rare earth **ftw**-MOF platform offers the potential to assess the effect of pore functionality and size on gas adsorption *via* ligand functionalization and/or expansion.





Redox Active Quinoid Ligands; Where Do Electrons Go and Why?



4118

4124



Prx I decamer
Triptolide Withaferin A Celastrol
Image: Construction of the second second

Capping nanoparticles with graphene quantum dots for enhanced thermoelectric performance

Yuantong Liang, Chenguang Lu,^{*} Defang Ding, Man Zhao, Dawei Wang, Chao Hu, Jieshan Qiu, Gang Xie^{*} and Zhiyong Tang^{*}

The general capability of graphene quantum dots to serve as capping ligands exchanging native organic stabilizers for various types of semiconductor nanoparticles affords the opportunity to engineer functional nanocomposites with remarkable thermoelectric properties.

Revealing the thermodynamic driving force for ligand-based reductions in quinoids; conceptual rules for designing redox active and non-innocent ligands

G. Skara, B. Pinter,* P. Geerlings and F. De Proft*

The easy reduction of quinoid ligands is driven thermodynamically by superior M–L electrostatics and σ -bonding in the reduced form.

Insights into the structure-photoreactivity relationships in well-defined perovskite ferroelectric KNbO₃ nanowires

Tingting Zhang, Wanying Lei, Ping Liu, José A. Rodriguez, Jiaguo Yu, Yang Qi, Gang Liu^{*} and Minghua Liu^{*}

1D perovskite-type orthorhombic KNbO₃ nanowires display RhB photodegradation about two-fold as large as their monoclinic counterparts and a synergy between ferroelectric polarization and electronic structure in photoreactivity enhancement is uncovered.

Natural products triptolide, celastrol, and withaferin A inhibit the chaperone activity of peroxiredoxin I

Qian Zhao, Yu Ding, Zhangshuang Deng, On-Yi Lee, Peng Gao, Pin Chen, Rebecca J. Rose, Hong Zhao, Zhehao Zhang, Xin-Pei Tao, Albert J. R. Heck, Richard Kao and Dan Yang^{*}

The natural products triptolide, withaferin A and celastrol have been discovered to be novel Prx I chaperone inhibitors using synthetic chemical probes.

Solid-phase synthesis provides a modular, lysine-based platform for fluorescent discrimination of nitroxyl and biological thiols

Andrei Loas, Robert J. Radford, Alexandria Deliz Liang and Stephen J. Lippard*

A synthetically facile solid-phase approach yields fluorescent Cu(\mathfrak{n})-based lysine conjugates which selectively detect nitroxyl and thiols in live cells.

4141

Taming C₆₀ fullerene: tuning intramolecular photoinduced electron transfer process with subphthalocyanines

M. Rudolf, O. Trukhina, J. Perles, L. Feng, T. Akasaka,* T. Torres* and D. M. Guldi*

Two subphthalocyanine $-C_{60}$ fullerene electron donor-acceptor conjugates have been prepared from electron deficient subphthalocyanines and C_{60} , with evidence of an ultrafast oxidative electron transfer from C_{60} to the subphthalocyanines.

4148

Assessing the exchange coupling in binuclear lanthanide(\square) complexes and the slow relaxation of the magnetization in the antiferromagnetically coupled Dy₂ derivative

C. Y. Chow, H. Bolvin, V. E. Campbell, R. Guillot, J. W. Kampf, W. Wernsdorfer, F. Gendron, J. Autschbach, V. L. Pecoraro^{*} and T. Mallah^{*}

Two relaxation processes of the magnetization in an antiferromagnetically coupled Dy_2 metallacrown-based complex.

4160

Acid/base-regulated reversible electron transfer disproportionation of N–N linked bicarbazole and biacridine derivatives

Palash Pandit, Koji Yamamoto, Toshikazu Nakamura, Katsuyuki Nishimura, Yuki Kurashige, Takeshi Yanai, Go Nakamura, Shigeyuki Masaoka, Ko Furukawa, Yumi Yakiyama, Masaki Kawano and Shuhei Higashibayashi^{*}

New acid/base-responsive organic compounds were discovered to undergo electron transfer disproportionation.













N BF4

LIHMDS

Non-covalent catalysis

EWG

EWG= NO2 or COR

R²= aryl or alkyl

 $R^3 = CF_3 \text{ or } H$

D

R²SR¹

S containing cent

up to 98% vield. 99% ee

R3

Palladium-catalyzed reductive coupling of phenols with anilines and amines: efficient conversion of phenolic lignin model monomers and analogues to cyclohexylamines

Zhengwang Chen, Huiying Zeng, Hang Gong, Haining Wang and Chao-Jun Li*

A highly efficient Pd-catalyzed direct coupling of phenolic lignin model monomers and analogues with anilines to give cyclohexylamines using sodium formate as hydrogen donor is described.

Organocatalytic asymmetric chlorinative dearomatization of naphthols

Qin Yin, Shou-Guo Wang, Xiao-Wei Liang, De-Wei Gao, Jun Zheng and Shu-Li You*

A highly enantioselective chlorinative dearomatization of 1-naphthol and 2-naphthols was realized for the first time, providing chiral naphthalenones with a Cl-containing all-substituted stereocenter in excellent yields and enantioselectivity (up to 97% yield and 96% ee).

Highly enantioselective sulfa-Michael addition reactions using *N*-heterocyclic carbene as a non-covalent organocatalyst

Jiean Chen, Sixuan Meng, Leming Wang, Hongmei Tang and Yong Huang $\!\!\!\!\!^{\star}$

Enantioselective asymmetric sulfa-Michael addition (SMA) reactions using a chiral *N*-heterocyclic carbene as a non-covalent organocatalyst.

4190

4184

R¹SH

broad scop



pH-responsive and switchable triplex-based DNA hydrogels

Jiangtao Ren, Yuwei Hu, Chun-Hua Lu, Weiwei Guo, Miguel Angel Aleman-Garcia, Francesco Ricci and Itamar Willner*

pH-responsive DNA hydrogels based on Hoogsteen CG \cdot C^+ or TA \cdot T triplex structures undergo reversible pH-induced hydrogel/solution transitions.

Charge transfer *versus* molecular conductance: molecular orbital symmetry turns quantum interference rules upside down

Natalie Gorczak, Nicolas Renaud, Simge Tarkuç, Arjan J. Houtepen, Rienk Eelkema, Laurens D. A. Siebbeles and Ferdinand C. Grozema^{*}

Molecular orbital symmetry considerations can strongly affect the nature of quantum interference effects in charge transfer.

4207

Vermicious thermo-responsive Pickering emulsifiers

K. L. Thompson, L. A. Fielding, O. O. Mykhaylyk,* J. A. Lane, M. J. Derry and S. P. Armes*

Thermo-responsive vermicious (or worm-like) diblock copolymer nanoparticles prepared directly in *n*-dodecane are used to stabilise water-in-oil Pickering emulsions.

4215

The A β 40 and A β 42 peptides self-assemble into separate homomolecular fibrils in binary mixtures but cross-react during primary nucleation

Risto Cukalevski, Xiaoting Yang, Georg Meisl, Ulrich Weininger, Katja Bernfur, Birgitta Frohm, Tuomas P. J. Knowles and Sara Linse*

Reaction network starting from monomer mixtures of A β 40 and A β 42. Interaction at the level of primary nucleation only accelerates A β 40 fibril formation. Separate fibrils form as secondary nucleation and elongation are highly specific.

4234

A pH-responsive soluble polymer-based homogeneous system for fast and highly efficient *N*-glycoprotein/glycopeptide enrichment and identification by mass spectrometry

Haihong Bai, Chao Fan, Wanjun Zhang, Yiting Pan, Lin Ma, Wantao Ying, Jianhua Wang, Yulin Deng, Xiaohong Qian* and Weijie Qin*

A homogeneous reaction system was developed for facile and highly efficient enrichment of biomolecules by exploiting the reversible self-assembly of a stimuli-responsive polymer.











Diastereodivergent organocatalysis for the asymmetric synthesis of chiral annulated furans

Charlie Verrier and Paolo Melchiorre*

Stereoselective methods to prepare chiral annulated furans are reported. Complementary organocatalytic systems ensure access to all possible stereoisomeric products.

4247



4255



Microdialysis SPR: diffusion-gated sensing in blood

Julien Breault-Turcot and Jean-Francois Masson*

Chemical measurements are rarely performed in crude blood due to the poor performance of sensors and devices exposed to biofluids.

Consecutive C-F bond activation and C-F bond formation of heteroaromatics at rhodium: the peculiar role of $FSi(OEt)_3$

A. L. Raza and T. Braun*

C–F activation reactions for a silyl complex gave fluorosilane and Rh pyridyl complexes. In consecutive reactions, the fluorosilane can act as a fluoride source and a regeneration of the C–F bond occurs by Si–F bond cleavage. This sets back the C–F bond cleavage reaction with consequences for the overall chemoselectivity of the activation reactions.

4261



Hyperpolarization of amino acid derivatives in water for biological applications

S. Glöggler, S. Wagner and L.-S. Bouchard*

We report on the successful synthesis and hyperpolarization of N-unprotected α -amino acid ethyl propionate esters and extensively, on an alanine derivative hyperpolarized by PHIP (4.4 \pm 1.0% ¹³C-polarization), meeting required levels for *in vivo* detection.

Strong circularly polarized luminescence from the supramolecular gels of an achiral gelator: tunable intensity and handedness

Zhaocun Shen, Tianyu Wang,* Lin Shi, Zhiyong Tang and Minghua Liu*

Supramolecular gels formed by an achiral gelator emit strong circularly polarized luminescence with tunable intensity and handedness.

4273

Enantioselective annulation of enals with 2-naphthols by triazolium salts derived from L-phenylalanine

Guo-Tai Li, Qing Gu and Shu-Li You*

The annulation reaction between enals and 2-naphthols catalyzed by a novel NHC affords enantioenriched β -arylsplitomicins in good yields and enantioselectivity.

4279

Copper-catalyzed diamination of unactivated alkenes with hydroxylamines

Kun Shen and Qiu Wang*

A copper-catalyzed regio- and stereoselective diamination of unactivated alkenes has been developed with O-acylhydroxylamines as electrophilic nitrogen sources and oxidants.



4284

Luminescence switch-on detection of protein tyrosine kinase-7 using a G-quadruplex-selective probe

Sheng Lin, Wei Gao, Zeru Tian, Chao Yang, Lihua Lu, Jean-Louis Mergny,* Chung-Hang Leung and Dik-Lung Ma*

A novel luminescent G-guadruplex-selective iridium(III) complex was employed in a G-quadruplex-based detection assay for PTK7.















lactam and imidazolidinone-containing 1.2-diamine products

N-N

EDGE ARTICLES



Iron catalyzed CO₂ hydrogenation to formate enhanced by Lewis acid co-catalysts

Yuanyuan Zhang, Alex D. MacIntosh, Janice L. Wong, Elizabeth A. Bielinski, Paul G. Williard, Brandon Q. Mercado, Nilay Hazari^{*} and Wesley H. Bernskoetter^{*}

Iron/Lewis acid co-catalysts hydrogenate to CO_2 to formate with unprecedented turnover for a first row transition metal catalyst.

Homochiral self-assembly of biocoordination polymers: anion-triggered helicity and absolute configuration inversion

Nadia Marino, Donatella Armentano,* Emilio Pardo,* Julia Vallejo, Francesco Neve, Leonardo Di Donna and Giovanni De Munno

The templating roles of ClO_4^- and $CF_3SO_3^-$ allow control and reversible inversion of the chirality of nucleotide-based copper(II) helices. These results hold great potential for developing responsive materials.

Low temperature ionic conductor: ionic liquid incorporated within a metal-organic framework

Kazuyuki Fujie,* Kazuya Otsubo, Ryuichi Ikeda, Teppei Yamada and Hiroshi Kitagawa*

An ionic liquid incorporated into micropores of a metal– organic framework showed higher ionic conductivity than bulk ionic liquid at low temperature because of the absence of marked freezing transition.

Simple electrochemical sensing of attomolar proteins using fabricated complexes with enhanced surface binding avidity

Chao Li, Xiaoxi Li, Luming Wei, Muyun Liu, Yangyang Chen and Genxi Li $\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!$

Target molecules selectively equipped with proximity probes can autonomously cleave substrates on the electrode surface, allowing quantification of proteins at attomolar concentrations with one-step incubation.





4306



4311



Target-driven DNA association to initiate cyclic assembly of hairpins for biosensing and logic gate operation

Yuehua Guo, Jie Wu and Huangxian Ju*

Target-driven DNA association is designed for initiating the cyclic assembly of hairpins for target detection and logic gate operation.



Mechanism of the cooperative Si-H bond activation at Ru-S bonds

Timo Stahl, Peter Hrobárik,* C. David F. Königs, Yasuhiro Ohki, Kazuyuki Tatsumi, Sebastian Kemper, Martin Kaupp, Hendrik F. T. Klare* and Martin Oestreich*

The heterolytic splitting of hydrosilanes by ruthenium(II) thiolates is illuminated by a combined spectroscopic, crystallographic, and computational analysis.





4335

A structural remedy toward bright dipolar fluorophores in aqueous media

S. Singha, D. Kim, B. Roy, S. Sambasivan, H. Moon, A. S. Rao, J. Y. Kim, T. Joo,* J. W. Park, Y. M. Rhee,* T. Wang, K. H. Kim,* Y. H. Shin, J. Jung* and K. H. Ahn*

Structural factors governing the poor emission of dipolar dyes in aqueous media are identified, leading to new acedan derivatives with brighter fluorescence and enhanced two-photon properties.

4343

ATP-triggered biomimetic deformations of bioinspired receptor-containing polymer assemblies

Qiang Yan and Yue Zhao*

A block copolymer can recognize ATP through bioinspired receptors to initiate a series of deformation and morphological transitions of the polymer assemblies.











Synthesis of open-mouthed, yolk-shell Au@AgPd nanoparticles with access to interior surfaces for enhanced electrocatalysis

Qiurong Shi, Peina Zhang, Yijing Li, Haibing Xia,* Dayang Wang and Xutang Tao

Open-mouthed, yolk-shell Au@AgPd nanoparticles are successfully produced *via* galvanic replacement reaction in water at room temperature.



How important are dispersion interactions to the strength of aromatic stacking interactions in solution?

Jungwun Hwang, Brent E. Dial, Ping Li, Michael E. Kozik, Mark D. Smith and Ken D. Shimizu*

The similarity of aromatic stacking energies in solution for varying sized surfaces suggests that dispersion interactions are a minor contributor.



Rapid access to phospholipid analogs using thiol-yne chemistry

Cun Yu Zhou, Haoxing Wu and Neal Krishna Devaraj*

Membrane-forming phospholipids analogs can be rapidly formed through use of thiol-yne click chemistry.

CORRECTION

4373

Correction: Modulating the electron-transfer properties of a mixed-valence system through host-guest chemistry

Ahmed Zubi, Ashley Wragg, Simon Turega, Harry Adams, Paulo J. Costa, Vítor Félix* and Jim A. Thomas*