Author Profile

"If I were not a scientist, I would be missing out. What I look for first in a publication is something beautiful (structure, concept, or result). …"
This and more about D. A. Leigh can be found on page 7628.

News


R. van Grondelle


H. S. Overkleeft


G. H. Robinson

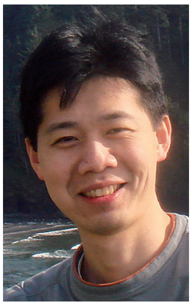

O. Steinbock


M. E. Thompson


G. Thornton


I. Wachs


J. S. Figueroa


S.-Y. Liu

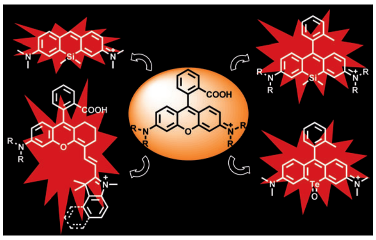

S. R. Little


S. Herzon

Books

Highlights

Fluorescent Probes



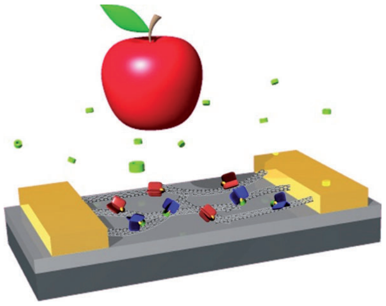
Probes to dye for: Rhodamine-inspired Si-pyronine, Si-rhodamine, Te-rhodamine, and Changsha NIR dyes have been developed recently. These dyes show fluorescence in the far-red to near-infrared region, while retaining the advantages of the original rhodamines, such as high fluorescence quantum yield, tolerance to photobleaching, good water solubility, and exhibit great potential for biological application.

Nanosensors

M. Ding, A. Star* ________ **7637 – 7638**

Selecting Fruits with Carbon Nanotube Sensors

Sensor strategy bears fruit: A nature-inspired Cu^I complex was employed to fabricate single-walled carbon nanotube sensors that can selectively detect ethylene gas at concentrations as low as 0.5 ppm. Such nanosensors may be used to monitor ethylene gas emitted from fruits to monitor their ripening.

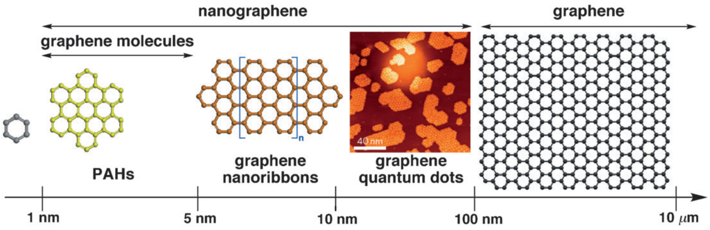


Minireviews

Graphene Synthesis

L. Chen, Y. Hernandez, X. Feng,*
K. Müllen* ____________ **7640 – 7654**

From Nanographene and Graphene Nanoribbons to Graphene Sheets: Chemical Synthesis



Of all shapes and sizes: Precise control over graphene synthesis is crucial for probing their fundamental physical properties and introduction into promising applications. In this Minireview, the recent progress that has led to the successful chemical synthesis of graphene with a range of different sizes and chemical compositions based on both top-down and bottom-up strategies is highlighted (see figure).

Reviews

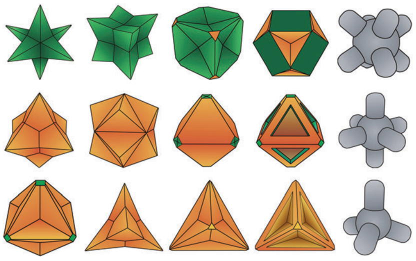
Concave Nanocrystals

H. Zhang, M. Jin, Y. Xia* ___ **7656 – 7673**

Noble-Metal Nanocrystals with Concave Surfaces: Synthesis and Applications

Inside Cover

Multifaceted materials: Many efforts have recently been devoted to the synthesis of noble-metal nanocrystals with concave surfaces. Their unique properties are enabled by high-index facets, surface cavities, and sharp corners/edges. A brief account is given of recent developments, with a focus on the growth mechanisms and enhanced catalytic/electrocatalytic properties.



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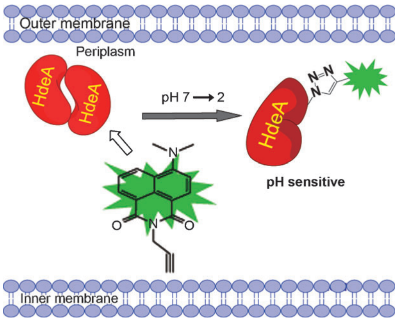
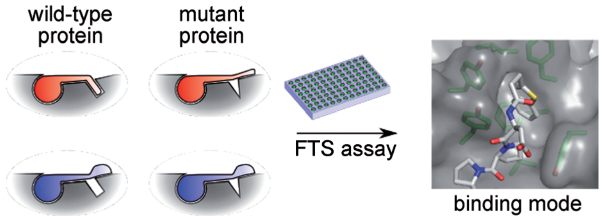
Protein-Based pH Sensor

Frontispiece



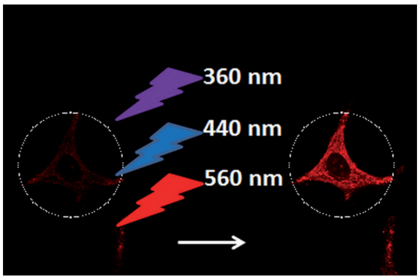
Live-cell pH measurements: An environment-sensitive fluorophore (green) was site-specifically introduced on HdeA, an acid-resistant chaperone showing pH-mediated conformational changes under low pH conditions. A survey of the attachment sites led to the discovery of one position on HdeA at which the attached fluorophore showed a strong fluorescence increase upon acidification.

Protein–Ligand Interactions



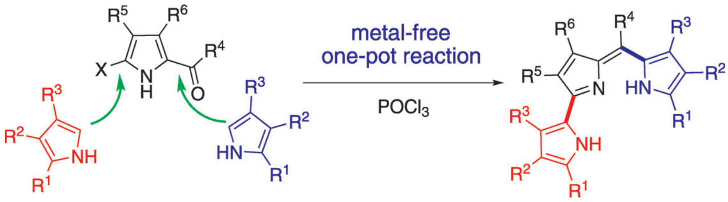
Probing the pocket: A high-throughput fluorescence-based thermal shift (FTS) assay utilized different forms of a protein (in gray) to establish the binding mode of a ligand (see picture). The assay serves in the rapid evaluation of structure–activity binding-mode relationships for a series of ligands of Plk1, an important target of anticancer therapy.

Selective Photolysis



Falling apart, on cue: Signaling pathways often display a profound spatiotemporal component that is best studied using light-activatable reagents. Three separate photolabile moieties that can be distinguished based upon their response to three distinct wavelengths (360, 440, and 560 nm) have been synthesized and evaluated. This tri-color system is also applied to imaging in microwells and HeLa cells (see picture).

Synthetic Methods



Three for one: Pyrrolyldipyrromethenes having different functional groups were efficiently synthesized from $POCl_3$-promoted condensations between 5-chloro-2-formylpyrrole or isoindole derivatives and suitable pyrrole or indole fragments through a novel nucleophilic aromatic substitution of the initially formed protonated azafulvene rings.

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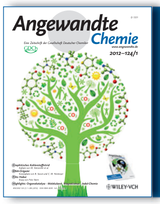

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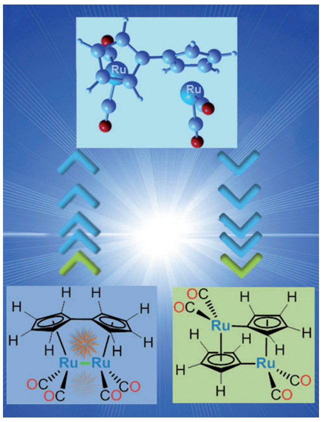

Caught in the light: The fulvalene diruthenium complex shown on the left side of the picture captures sun light, causing initial Ru–Ru bond rupture to furnish a long-lived triplet biradical of syn configuration. This species requires thermal activation to reach a crossing point (middle) into the singlet manifold on route to its thermal storage isomer on the right through the anti biradical.

Photochemistry

M. R. Harpham, S. C. Nguyen, Z. Hou,
J. C. Grossman, C. B. Harris,*
M. W. Mara, A. B. Stickrath, Y. Kanai,*
A. M. Kolpak, D. Lee
D.-J. Liu, J. P. Lomont, K. Moth-Poulsen,
N. Vinokurov, L. X. Chen,*
K. P. C. Vollhardt* ———— **7692 – 7696**

X-ray Transient Absorption and Picosecond IR Spectroscopy of Fulvalene(tetracarbonyl)diruthenium on Photoexcitation

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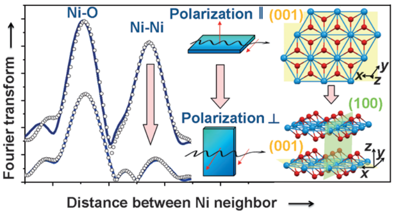
Surface-dependent precipitation: The adsorption of Ni^{II} complexes in aqueous solution on (0001) and (1$\bar{1}$02) α-Al$_2$O$_3$ single-crystal surfaces has been studied (see the X-ray absorption spectra obtained for parallel and perpendicular polarization directions). The use of planar model systems emphasizes the crucial role of the Al$_2$O$_3$ orientation for Ni dispersion with practical implications in catalyst preparation procedures.



Surface Chemistry

A. Tougerti, I. Llorens, F. D'Acapito,
E. Fonda, J.-L. Hazemann, Y. Joly,
D. Thiaudière, M. Che,
X. Carrier* ———— **7697 – 7701**

Surface Science Approach to the Solid–Liquid Interface: Surface-Dependent Precipitation of Ni(OH)$_2$ on α-Al$_2$O$_3$ Surfaces

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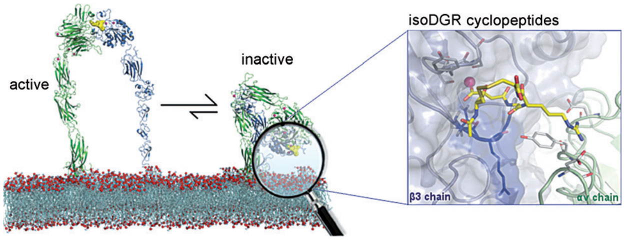

Ain't got that swing(-out): The cyclopeptide isoDGR is emerging as a new αvβ3 integrin binding motif. Agreement between the results of computational and biochemical studies reveals that isoDGR-containing cyclopeptides are true αvβ3 integrin antagonists that block αvβ3 in its inactive conformation (see scheme). isoDGR-based ligands may give αvβ3 antagonists without paradoxical effects.

Integrin Cyclopeptides

M. Ghitti, A. Spitaleri, B. Valentinis,
S. Mari, C. Asperti, C. Traversari,
G.-P. Rizzardi,* G. Musco* **7702 – 7705**

Molecular Dynamics Reveal that isoDGR-Containing Cyclopeptides Are True αvβ3 Antagonists Unable To Promote Integrin Allostery and Activation

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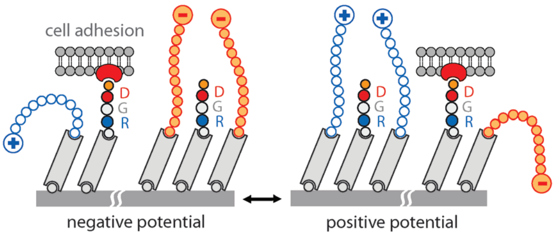


Smart surfaces presenting both antifouling molecules with a charged functional group at their distal end, and molecules that are terminated by RGD peptides for cell adhesion, were fabricated and characterized (see picture). By applying potentials of +300 or −300 mV, the surfaces could be dynamically switched to make the peptide accessible or inaccessible to cells.

Surface Chemistry

A. Ng, A. Magenau, S. Ngalim, S. Ciampi,
M. Chockalingham, J. Harper, K. Gaus,
J. Gooding* ———— **7706 – 7710**

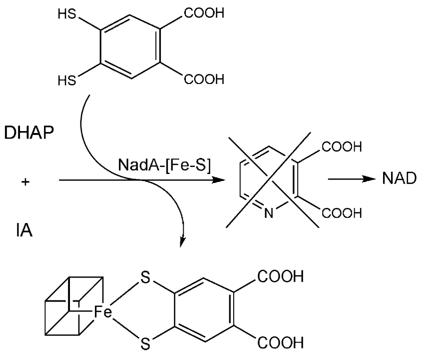
Using an Electrical Potential to Reversibly Switch Surfaces between Two States for Dynamically Controlling Cell Adhesion

NAD Biosynthesis

A. Chan, M. Clémancey, J. M. Mouesca, P. Amara, O. Hamelin, J. M. Latour, S. Ollagnier de Choudens* _ **7711 – 7714**

Studies of Inhibitor Binding to the [4Fe-4S] Cluster of Quinolinate Synthase

Stop for NadA! A [4Fe-4S] enzyme, NadA, catalyzes the formation of quinolinic acid in de novo nicotinamide adenine dinucleotide (NAD) biosynthesis. A structural analogue of an intermediate, 4,5-dithiohydroxyphthalic acid (DTHPA), has an in vivo NAD biosynthesis inhibiting activity in *E. coli*. The inhibitory effect can be explained by the coordination of DTHPA thiolate groups to a unique Fe site of the NadA [4Fe-4S] cluster.

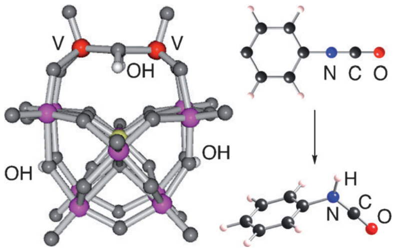


Reactive Intermediates

K. Uehara, K. Fukaya, N. Mizuno* ______ **7715 – 7718**

Reactive N-Protonated Isocyanate Species Stabilized by Bis(μ-hydroxo)-divanadium(IV)-Substituted Polyoxometalate

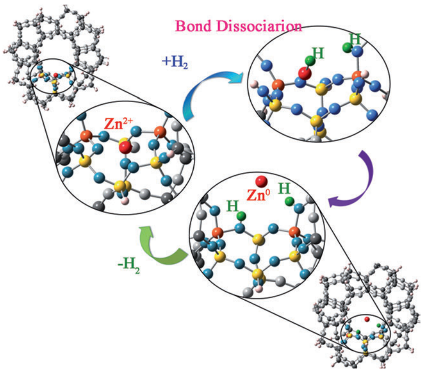
O- or N-protonated? The bis(μ-hydroxo)-divanadium(IV)-substituted γ-Keggin-type polyoxometalate (see picture, left) $(TBA)_4[\gamma\text{-}SiV^{IV}_2W_{10}O_{36}(\mu\text{-}OH)_4]$ (TBA = tetra(*n*-butyl)ammonium) was synthesized and characterized by X-ray crystallography. Its reaction with phenyl isocyanate gave $(TBA)_4[\gamma\text{-}SiV^{IV}_2W_{10}O_{38}(\mu\text{-}OH)_2\text{-}(PhNHCO)_2]$, which contains two N-protonated phenyl isocyanate species and catalyzes the cyclotrimerization of phenyl isocyanate.



H_2 Activation in Zeolites

A. Oda, H. Torigoe, A. Itadani, T. Ohkubo, T. Yumura, H. Kobayashi, Y. Kuroda* ______ **7719 – 7723**

Unprecedented Reversible Redox Process in the ZnMFI—H_2 System Involving Formation of Stable Atomic Zn^0

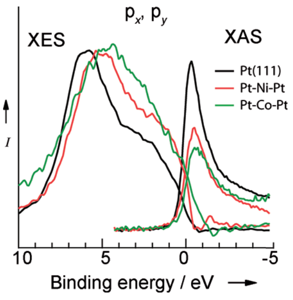


In its element: Zn^{2+} at the M7 site of MFI-type zeolites activates H_2, via ZnH and OH species, and leads to Zn^0 species. The Zn^0 species returns to its original state, a Zn^{2+} ion, upon evacuation of the zeolite at 873 K (see picture). The formation of the Zn^0 species is supported by DFT calculations.

Heterogeneous Catalysis

T. Anniyev, S. Kaya,* S. Rajasekaran, H. Ogasawara, D. Nordlund, A. Nilsson ______ **7724 – 7728**

Tuning the Metal–Adsorbate Chemical Bond through the Ligand Effect on Platinum Subsurface Alloys

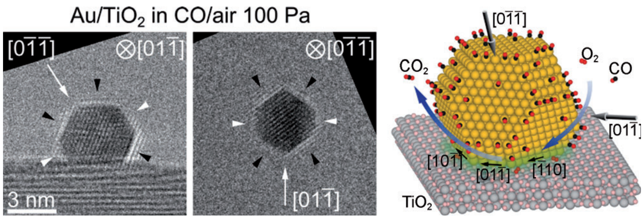


Scratching beneath the surface: $Pt\text{-}M_{3d}\text{-}Pt(111)$ (M_{3d} = Co, Ni) bimetallic subsurface alloys have been designed to show the ligand effect tunes reactivity in oxygen and hydrogen adsorption systems. The platinum–oxygen bond order was investigated by oxygen atom projection in the occupied and unoccupied space using X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS).

Gold Nanoparticles

Y. Kuwauchi, H. Yoshida, T. Akita,
M. Haruta, S. Takeda* ____ **7729 – 7733**

Intrinsic Catalytic Structure of Gold Nanoparticles Supported on TiO_2

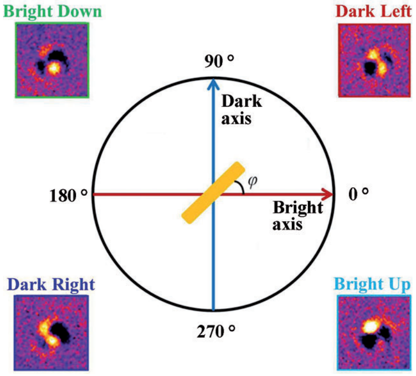


Despite the fragility of TiO_2 under electron irradiation, the intrinsic structure of Au/TiO_2 catalysts can be observed by environmental transmission electron microscopy. Under reaction conditions (CO/air 100 Pa), the major {111} and {100} facets of the gold nanoparticles are exposed and the particles display a polygonal interface with the TiO_2 support bounded by sharp edges parallel to the ⟨110⟩ directions.

Nanoparticle Tracking

L. Xiao, J. W. Ha, L. Wei, G. Wang,
N. Fang* ____________ **7734 – 7738**

Determining the Full Three-Dimensional Orientation of Single Anisotropic Nanoparticles by Differential Interference Contrast Microscopy



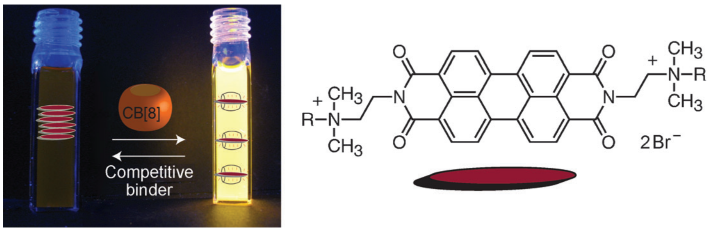
Keeping track: By combining differential interference contrast (DIC) image pattern recognition with DIC polarization anisotropy, the exact full three-dimensional angular information of individual tilted gold nanorods positioned in the focal plane of the objective lens can be readily determined. The angular rotational modes and kinetics of individual in-focus gold nanorods can thus be resolved dynamically.

Dye Deaggregation

F. Biedermann, E. Elmalem, I. Ghosh,
W. M. Nau,
O. A. Scherman* ________ **7739 – 7743**

Strongly Fluorescent, Switchable Perylene Bis(diimide) Host–Guest Complexes with Cucurbit[8]uril In Water

Back Cover

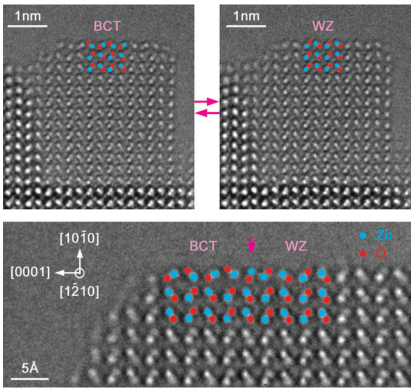


Supramolecular complexation of perylene bis(diimide) (PDI) dyes with the macrocyclic host cucurbit[8]uril (CB[8]) prevents self-aggregation of the dye molecules and enables their use as highly (photo)chemically stable, strongly-emitting fluorophores in water. The complexes are stimuli-responsive to binders and can be electrochemically cycled, leading to reversible on–off fluorescence switching and access to noncovalent formation of higher-order architectures in water.

Surface Chemistry

M. He, R. Yu, J. Zhu* ______ **7744 – 7747**

Reversible Wurtzite–Tetragonal Reconstruction in ZnO(10$\bar{1}$0) Surfaces

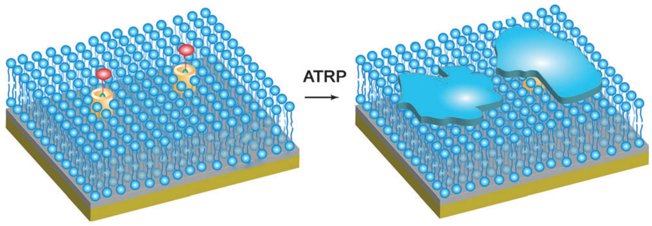


Bistable surface: The reversible phase transition between wurtzite (WZ) and body-centered-tetragonal (BCT) lattice was activated in ZnO(10$\bar{1}$0) surfaces and directly imaged at atomic scale by using aberration-corrected electron microscopy (see picture). A nucleation-growth mechanism for the surface reconstruction is further proposed based on observations and calculations of the WZ–BCT domain boundary.

Molecular Recognition

Y. Liu, M. C. Young, O. Moshe, Q. Cheng,*
R. J. Hooley* ______ **7748 – 7751**

A Membrane-Bound Synthetic Receptor that Promotes Growth of a Polymeric Coating at the Bilayer–Water Interface

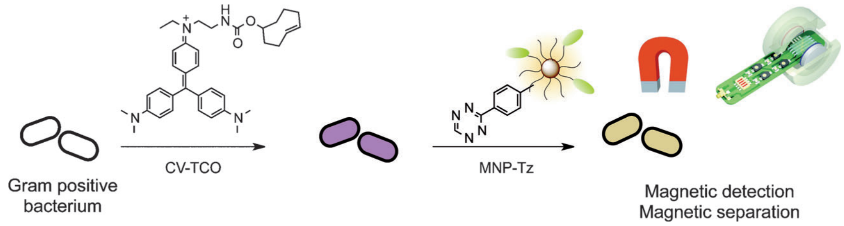


Primed for action: Atom-transfer radical polymerization (ATRP) can be promoted at a bilayer–water interface by anchoring initiator molecules (see scheme; red) in a membrane-bound synthetic receptor (yellow). The bilayer is formed on a calcinated nanofilm (gray) on a gold surface.

Biosensors

G. Budin, H. J. Chung, H. Lee,
R. Weissleder* ______ **7752 – 7755**

A Magnetic Gram Stain for Bacterial Detection



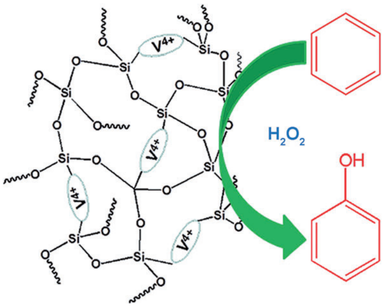
Magnetizing: Bacteria are often classified into Gram-positive and Gram-negative strains by staining with crystal violet (CV). The described bioorthogonal modification of CV with *trans*-cyclooctene (TCO) can be used to render Gram-positive bacteria magnetic with tetrazine-functionalized magnetic nanoparticles (MNP-Tz). This method allows class-specific automated magnetic detection and magnetic separation.

Benzene Hydroxylation

P. Borah, X. Ma, K. T. Nguyen,
Y. L. Zhao* ______ **7756 – 7761**

A Vanadyl Complex Grafted to Periodic Mesoporous Organosilica: A Green Catalyst for Selective Hydroxylation of Benzene to Phenol

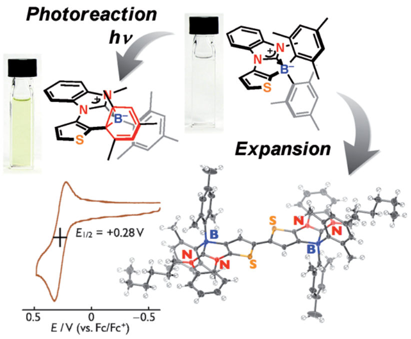
Selective benzene hydroxylation: A periodic mesoporous organosilica embedded with a vanadyl(IV) acetylacetonate complex has been synthesized through a co-condensation method. This system is a catalyst for direct hydroxylation of benzene to phenol, presenting a selectivity of 100% towards the phenol formation as well as an excellent catalytic recyclability (see scheme).



NHC–boranes

K. Nagura, S. Saito, R. Fröhlich,
F. Glorius,* S. Yamaguchi* **7762 – 7766**

N-Heterocyclic Carbene Boranes as Electron-Donating and Electron-Accepting Components of π-Conjugated Systems

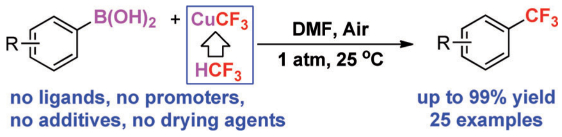


Give and take: The introduction of NHC–borane moieties to thiophene-based π skeletons endows a zwitterionic character, which makes the π system electron-donating, while the NHC ring acts as an electron-accepting moiety. The NHC–borane-substituted thiophene underwent a clean photoisomerization with a drastic color change, however, the expanded bithiophene derivatives were inert to this photoreaction, showed low oxidation potentials, and formed a slipped π-stacked array in the crystal.

Trifluoromethylation

P. Novák, A. Lishchynskyi,
V. V. Grushin* **7767 – 7770**

Fluoroform-Derived $CuCF_3$ for Low-Cost, Simple, Efficient, and Safe Trifluoromethylation of Aryl Boronic Acids in Air

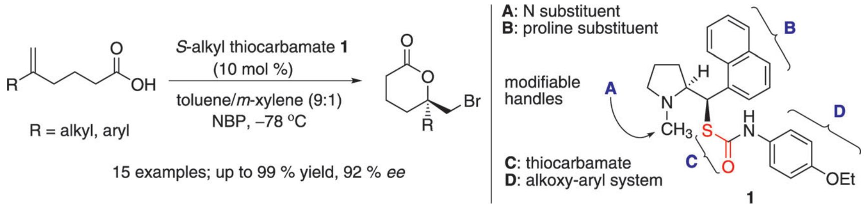


Easy does it: Aryl boronic acids undergo smooth and selective trifluoromethylation with low-cost fluoroform-derived $CuCF_3$ in DMF in non-dried air. The reaction occurs under mild conditions (1 atm, room temperature), exhibits unprecedented functional-group tolerance, and affords trifluoromethylated aromatic compounds in up to 99% yield.

Asymmetric Catalysis

X. Jiang, C. K. Tan, L. Zhou,
Y.-Y. Yeung* **7771 – 7775**

Enantioselective Bromolactonization Using an *S*-Alkyl Thiocarbamate Catalyst

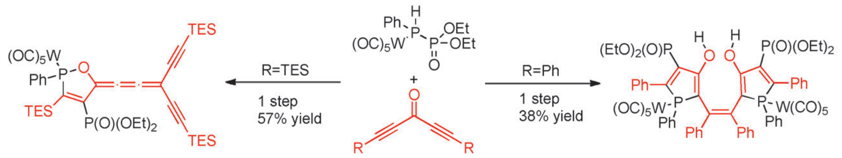


The apple never falls far from the tree: *S*-alkyl thiocarbamate **1** (see scheme, NBP = *N*-bromophthalimide) was prepared in high yield through a synthetic sequence involving a Newman–Kwart rearrangement of the corresponding *O*-alkyl thiocarbamates. Compound **1** was used to catalyze bromolactonization, thus providing enantioenriched δ-lactones in excellent yield and enantioselectivity.

Phosphaorganic Chemistry

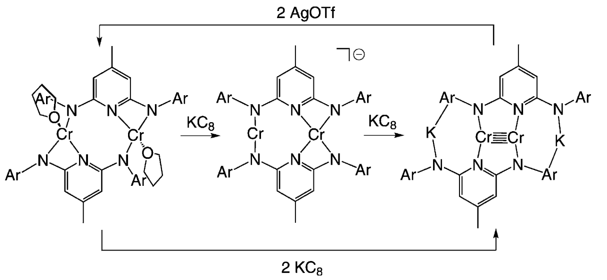
A. I. Arkhypchuk, M.-P. Santoni,
S. Ott* **7776 – 7780**

Cascade Reactions Forming Highly Substituted, Conjugated Phospholes and 1,2-Oxaphospholes



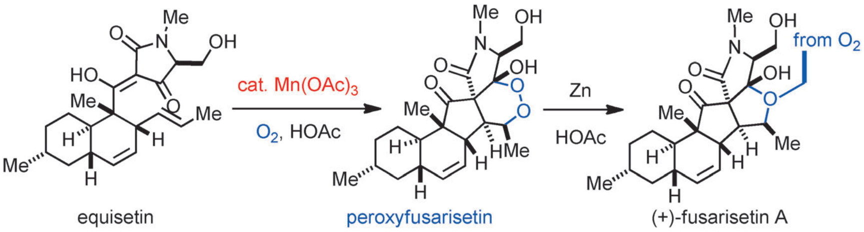
More than just a carbon copy: The reaction of a phospha-Wittig–Horner reagent with diacetylenic ketones (see scheme) results in a cascade of reactions that can lead to both an oxaphosphole-terminated cumulene system and an alkene-bridged bis-phosphole. The reaction outcome is determined by the nature of the acetylene termini, with phenyl groups stabilizing a carbene intermediate that dimerizes to give the bis-phosphole product.

Quintuple Bonding



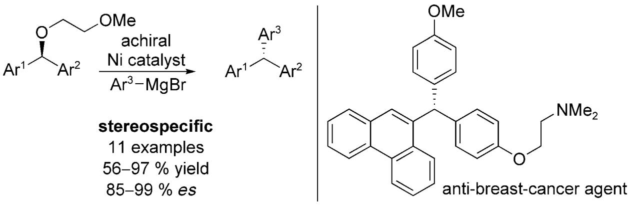
Give me five! Terdentate 2,6-diamidopyridyl ligands were used to stabilize the Cr–Cr quintuple bond and have made it possible to isolate and characterize not only the Cr–Cr quintuple-bonded complex, but also the mixed-valent intermediates ($\mathrm{Cr^{I}}$ and $\mathrm{Cr^{II}}$), which are important species in the formation of type I quintuple-bonded complexes.

Natural Products



Starting from equisetin, the asymmetric synthesis of (+)-fusarisetin A has been accomplished in a one-pot transformation including a biomimetic oxidation and an intramolecular Diels–Alder/Roskamp reaction. Peroxyfusarisetin is proposed as a plausible biosynthetic intermediate based on studies of the oxidation of equisetin.

Cross-Coupling

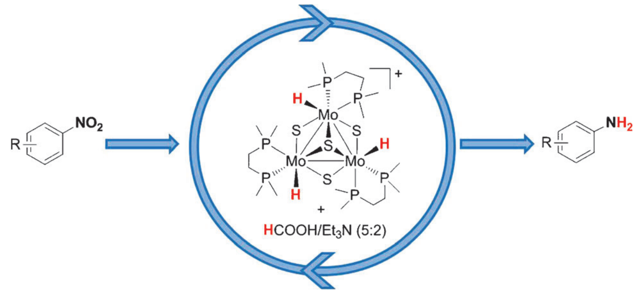


Coupling with inversion: Chiral diarylmethanol derivatives undergo a stereospecific nickel-catalyzed cross-coupling reaction with aryl Grignard reagents (see scheme). The reaction proceeds with inversion of configuration and high enantiospecificity. The method has been applied to the asymmetric synthesis of a triarylmethane-based anti-cancer compound.

Molybdenum Cluster Catalysis

I. Sorribes, G. Wienhöfer, C. Vicent,
K. Junge, R. Llusar,*
M. Beller* ———— 7794 – 7798

Chemoselective Transfer Hydrogenation to Nitroarenes Mediated by Cubane-Type Mo_3S_4 Cluster Catalysts

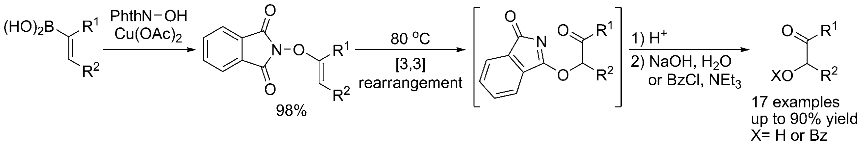


Chemoselective cubes: Cubane-type $[Mo_3S_4X_3(dmpe)_3]^+$ clusters (dmpe = 1,2-(bis)dimethylphosphinoethane), in combination with an azeotropic 5:2 mixture of HCOOH and NEt_3 as the reducing agent, act as selective cluster catalysts (X = H) or precatalysts (X = Cl) for the transfer hydrogenation of functionalized nitroarenes, without the formation of hazardous hydroxylamines.

Pericyclic Rearrangement

A. S. Patil, D.-L. Mo, H.-Y. Wang,
D. S. Mueller,
L. L. Anderson* ———— 7799 – 7803

Preparation of α-Oxygenated Ketones by the Dioxygenation of Alkenyl Boronic Acids

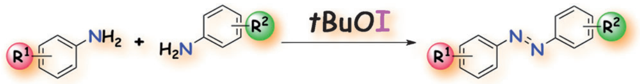


Two in two: Dioxygenation of alkenyl boronic acids has been achieved with *N*-hydroxyphthalimide. The two-step process involves etherification of an alkenyl boronic acid with *N*-hydroxyphthalimide followed by a [3,3] rearrangement. The dioxygenated product can then be hydrolyzed to form either the corresponding α-hydroxy ketone or the α-benzoyloxy ketone.

Synthetic Methods

Y. Takeda, S. Okumura,
S. Minakata* ———— 7804 – 7808

Oxidative Dimerization of Aromatic Amines using *t*BuOI: Entry to Unsymmetric Aromatic Azo Compounds



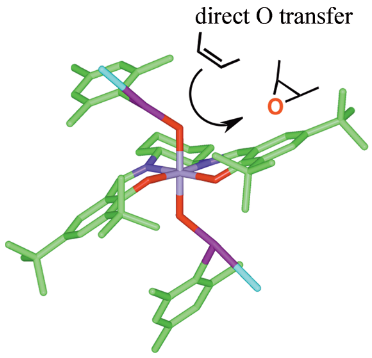
It's all the hype: An oxidative dimerization reaction of aromatic amines utilizing *tert*-butyl hypoiodite (*t*BuOI) under mild reaction conditions leads to aromatic azo compounds (see scheme). The method allows access to unsymmetric aromatic azo compounds, which are difficult to prepare by conventional synthetic methods, in a selective manner.

Oxygen Transfer

C. Wang, T. Kurahashi,
H. Fujii* ———— 7809 – 7811

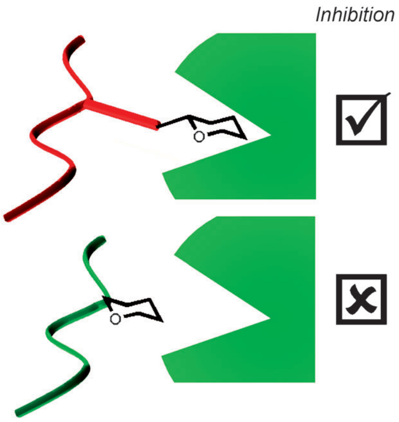
Structure and Reactivity of an Iodosylarene Adduct of a Manganese(IV)–Salen Complex

O transfer: The X-ray crystal structure of an iodosylarene adduct of a manganese(IV)–salen complex shows bis-iodosylarene coordination with a stepped conformation of the salen ligand. Spectroscopic characterization suggests that the complex maintains the same structure in solution. A reactivity study indicates that the manganese-bound iodosylarene can directly transfer an oxygen atom to substrate.

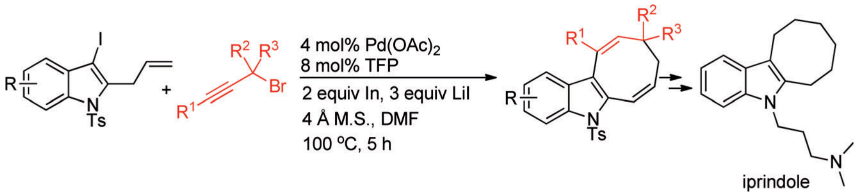


Glycopolymer Binding

Probing the depths: A tandem post-polymerization modification strategy was used to systematically probe the multivalent inhibition of a bacterial toxin as a function of linker length (see scheme), carbohydrate density, and glycopolymer chain length. Guided by structural-biology information, the binding-pocket depth of the toxin was probed and used as a means to specifically improve inhibition of the toxin by the glycopolymer.



Heterocycles



Ring fusion: The Pd^0-catalyzed reaction of 2-allyl-3-iodo-1-tosyl-1*H*-indoles and propargylic bromides affords dihydrocycloocta[*b*]indoles (see scheme; M.S. = molecular sieves, TFP = tris(2-furyl)phosphine, Ts = 4-toluenemethanesulfonyl), and proceeds by carbon–carbon coupling, [1,5]-hydrogen migration, and electrocyclization. The newly established method was used to efficiently access iprindole.

DOI: 10.1002/anie.201204653

50 Years Ago . . .

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

Issue 8 in 1962 started with a Review by G. Wittig on small rings with carbon–carbon triple bonds, in particular the formation and reactions of benzyne (didehydrobenzene), which had been first postulated as intermediate by Wittig in 1942 and is still being exploited today. The issue of whether benzyne was a true intermediate or only a transition state was also addressed, and evidence that benzyne occurs as an intermediate in reactions, and in the gas phase was presented. A thermal synthesis of benzyne in a specially constructed apparatus led to its capture under high vacuum under argon, thus paving the way for further studies.

The preparation of 5-amino sugars was discussed in by H. Paulsen in a Communication. These compounds are of particular interest as they can transform into piperidinoses, which comprise a six-membered ring that contains a nitrogen atom. The amino sugars were prepared as their acetamido derivatives, and upon hydrolysis, the carbonyl group interacts with the free amino group to produce a 3-hydroxypyridine after spontaneous elimination of water and aromatization of a postulated piperidinose intermediate.

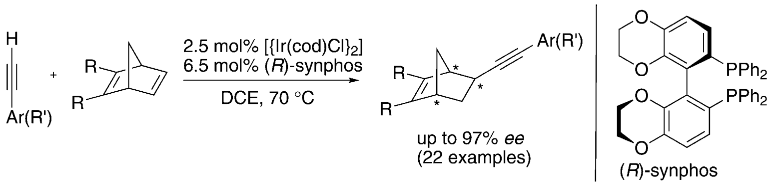
Angewandte Chemie has often published articles that use the results from further studies to dispute a previously reported claim, and a Communication by R. Huisgen and W. Edl opposed a statement made in 1927 that dibenzoyl peroxide can benzoxylate benzene in the presence of $AlCl_3$. They reported that phenyl benzoate is in fact obtained in both toluene and non-aromatic solvents and went on to describe how BF_3 in dichloromethane is a particularly suitable catalyst for the production of carboxylic esters from mixed diacyl peroxides. A mechanism was proposed that was consistent with independent studies that used $AlCl_3$ and an isotopically labeled peroxide, and were reported whilst the article was in press.

Read more in Issue 8/1962

Asymmetric Catalysis

B.-M. Fan,* Q.-J. Yang, J. Hu, C.-L. Fan,
S.-F. Li, L. Yu, C. Huang, W. W. Tsang,
F. Y. Kwong* ______ 7821 – 7824

Asymmetric Hydroalkynylation of Norbornadienes Promoted by Chiral Iridium Catalysts

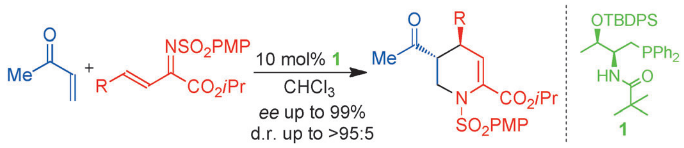


Across bonds: The first successful iridium-catalyzed asymmetric hydroalkynylation of nonpolar alkenes with good to excellent enantioselectivity is described (see scheme; cod = 1,5-cyclooctadiene, DCE = 1,2-dichloroethane). This catalytic system exhibits good functional group compatibility as NH$_2$, OH, Br, F, and SiMe$_3$ groups remain intact during the reaction.

Cyclization

Z. Shi, P. Yu, T. P. Loh,*
G. Zhong* ______ 7825 – 7829

Catalytic Asymmetric [4+2] Annulation Initiated by an Aza-Rauhut–Currier Reaction: Facile Entry to Highly Functionalized Tetrahydropyridines



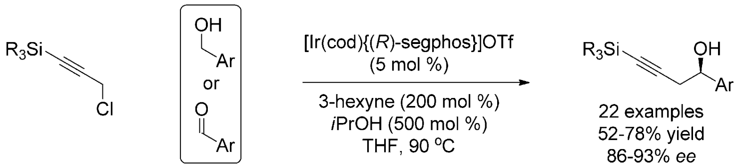
Under control: The first example of chiral amino phosphine catalysts for the title reaction between vinyl ketones and *N*-sulfonyl-1-aza-1,3-dienes has been developed. Under ambient conditions, this protocol provides straightforward access to densely functionalized, enantioenriched tetrahydropyridines with high levels of sterecontrol in good to excellent yields.

Inside Back Cover

Asymmetric Catalysis

S. K. Woo, L. M. Geary,
M. J. Krische* ______ 7830 – 7834

Enantioselective Carbonyl Propargylation by Iridium-Catalyzed Transfer Hydrogenative Coupling of Alcohols and Propargyl Chlorides

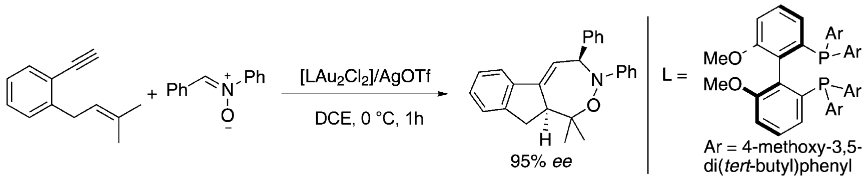


It takes alkynes! Exposure of propargyl chlorides to primary benzylic alcohols in the presence of [Ir(cod){(*R*)-segphos}]OTf (cod = 1,5-cyclooctadiene, segphos = 5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole, Tf = trifluoromethanesulfonyl) results in hydrogen exchange to give allenyliridium–aldehyde pairs that combine to form products of propargylation with high *ee* value (see scheme). The reaction can also be conducted using aldehydes.

Synthetic Methods

S. A. Gawade, S. Bhunia,
R.-S. Liu* ______ 7835 – 7838

Intermolecular Gold-Catalyzed Diastereo- and Enantioselective [2+2+3] Cycloadditions of 1,6-Enynes with Nitrones

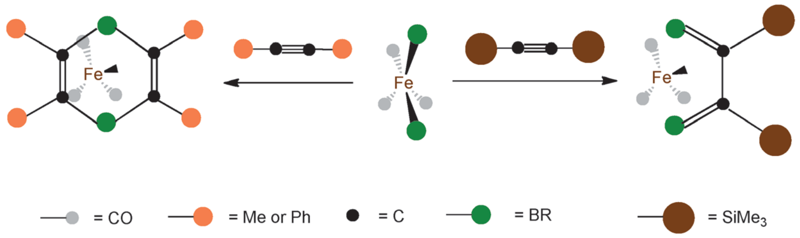


Going for gold: The title reaction has been developed and demonstrates a wide substrate scope with respect to the 1,6-enynes and nitrones (see scheme; DCE = 1,2-dichloroethane, Tf = trifluoromethanesulfonyl). The results for the enantioselective versions are also presented.

Borylene Transfer

H. Braunschweig,* Q. Ye, K. Radacki,
A. Damme ________ 7839 – 7842

Borylene Transfer from an Iron Bis(borylene) Complex: Synthesis of 1,4-Diboracyclohexadiene and 1,4-Dibora-1,3-Butadiene Complexes

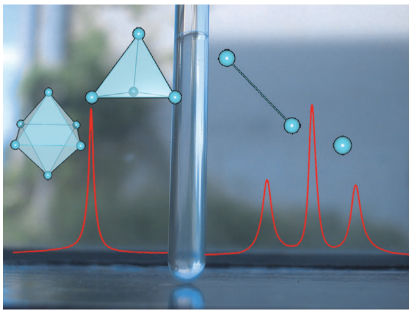


Diene to be made: By tuning the size of acetylenic substituents, 1,4-diboracyclohexadiene and unprecedented 1,4-dibora-1,3-butadiene complexes were generated in a controlled manner by borylene transfer from an iron bis(borylene) complex to alkynes (see scheme).

NMR Methods

A.-C. Pöppler, H. Keil, D. Stalke,*
M. John* ________ 7843 – 7846

^{7}Li Residual Quadrupolar Couplings as a Powerful Tool To Identify the Degree of Organolithium Aggregation



Lithium in the gel: The NMR spectroscopic properties of common organolithium and lithium amide reagents are investigated in the anisotropic environment of a stretched polystyrene (PS) gel. PS is stable towards reactive organometallic compounds and can be used at low temperatures. The residual quadrupolar couplings (RQCs) from a single ^{7}Li NMR spectrum can distinguish between high (hexamer, tetramer) and low (dimer, monomer) aggregation states (see scheme).

F_2 in Nature

J. Schmedt auf der Günne, M. Mangstl,
F. Kraus* ________ 7847 – 7849

Occurrence of Difluorine F_2 in Nature: In Situ Proof and Quantification by NMR Spectroscopy

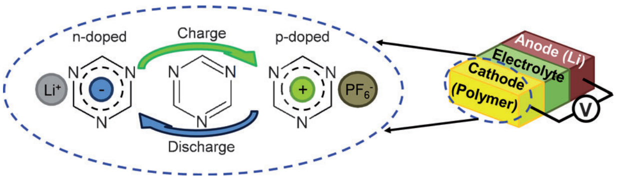
The most reactive chemical element, F_2, has been claimed not to occur in nature. First direct evidence from in situ NMR spectroscopy now proves that elemental F_2 indeed occurs in nature as an occlusion in “antozonite” (right in the picture), a variant of fluorite (CaF_2, left).

Front Cover

Porous Polymeric Frameworks

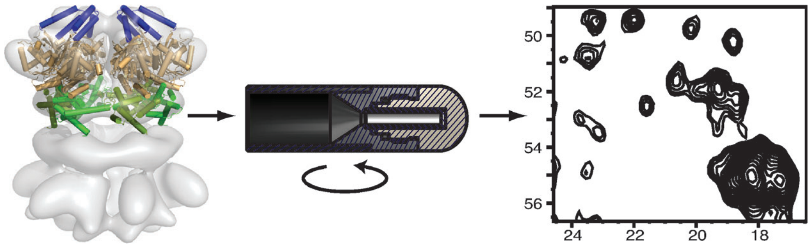
K. Sakaushi,* G. Nickerl, F. M. Wisser,
D. Nishio-Hamane, E. Hosono, H. Zhou,*
S. Kaskel, J. Eckert ________ 7850 – 7854

An Energy Storage Principle using Bipolar Porous Polymeric Frameworks



Packed with energy: Amorphous covalent triazine-based frameworks were used as a cathode material, with the aim of developing an energy storage principle that can deliver a 2–3 times higher specific energy than current batteries with a high rate capability. The material undergoes a unique Faradaic reaction, as it can be present in both a p-doped and an n-doped state (see picture).

Solid-State NMR Spectroscopy



Crystal clear: Preparing solid-state NMR samples that yield high-resolution spectra displaying high sensitivity is time-consuming and complicated. A sample of the 59 kDa protein DnaB, prepared simply by preparative centrifugation, provides spectra that are as good as the ones from carefully grown microcrystals.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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