VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

Author Profile

"If I won the lottery, I would be able to finally stop writing grants!
In my opinion, the word "scientist" means explorer …"
This and more about Michel R. Gagné can be found on page 11286.

News

C. R. Bertozzi

R. Metternich

J. A. Rogers

Obituaries

Books

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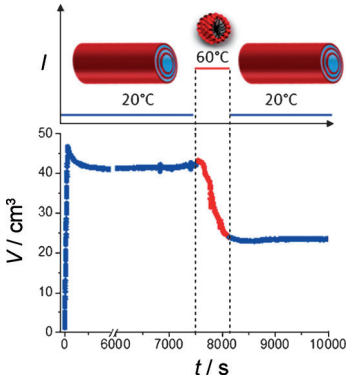
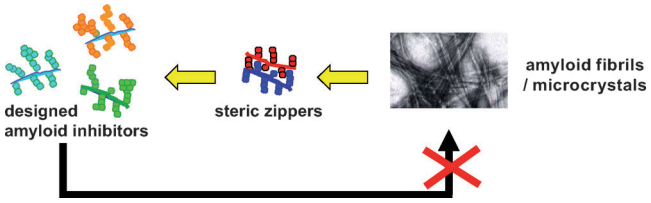
Highlights

Hold the foam! Smart foams with a tunable surface-to-volume ratio have numerous potential applications, including decontamination. Recently fatty acid aggregates, the stability of which can be tuned by an external stimulus, were described. The picture shows a plot of the foam volume of a temperature-dependent foam which undergoes supramolecular reorganization.





Zip code: A potentially general, computational design approach has been used to devise peptide inhibitors of protein aggregation into amyloid fibrils. The atomic structures of "steric zippers", which are formed by short fibril-forming segments of the amyloidogenic proteins, serve as templates. The validity of the approach is demonstrated by the design of inhibitors of amyloid formation associated with Alzheimer's disease pathology and HIV infectivity.

Minireviews

A tangled web: Semiochemicals and acylpolyamine toxins from spiders (see pictures) are unique biological probes and may even be considered potential therapeutic agents. In this Minireview a status update on the research regarding these interesting small molecules is presented.

For the USA and Canada:
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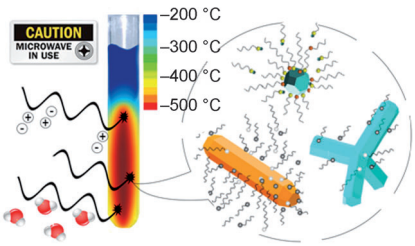
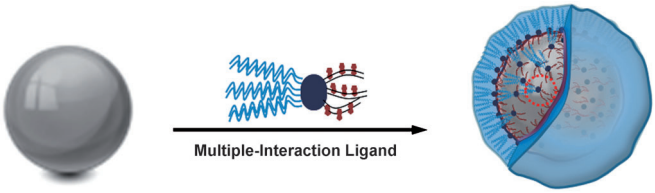
Reviews



If you can't stand the heat, get out of the kitchen: Direct volumetric and efficient heating by microwave irradiation enables the generation of colloidal nanocrystals in a fraction of the time required using conventional heating techniques (see picture). Among the advantages of this non-classical heating method is a great control of reaction temperature, allowing better versatility, reproducibility, and reduced processing times in the fabrication of high-quality nanocrystals.

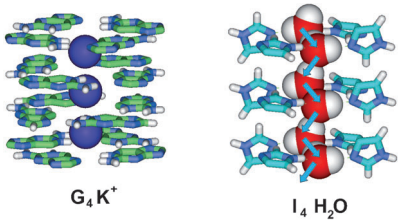
Microwave Chemistry

Communications



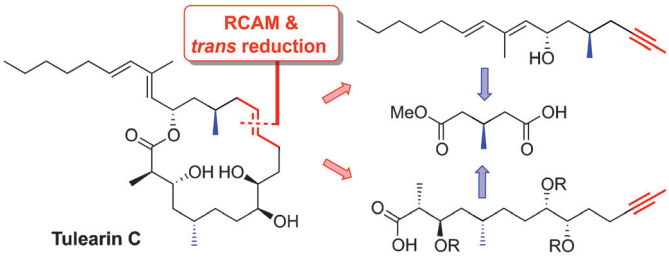
All bound up: A poly(L-3,4-dihydroxyphenylalanine)-based ligand converts hydrophobic nanoparticles into hydrophilic and biocompatible species through several binding modes. Nanoparticles functionalized with this ligand (see picture) are highly stable in various aqueous solutions. A successful in vivo MRI application using functionalized Fe_3O_4 nanoparticles confirmed their suitability for various biomedical applications.

Nanoparticles



Dipolar water wires stabilize quartets of ureido imidazole compounds (I-quartets) in a manner reminiscent of stabilization of guanine (G) quartets by cation templating (see picture).

Water Channels

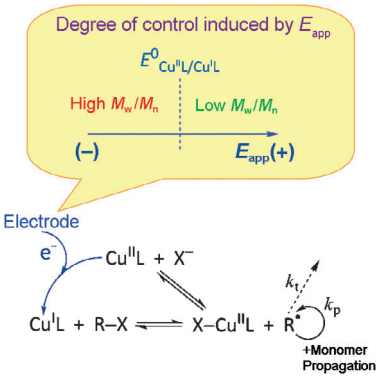


With the help of the smaller brother: Although alkyne metathesis will always be the little brother of alkene metathesis, it allows problems to be solved that are currently beyond reach of the more famous sibling. This notion is exemplified by the tulearin macrolides, which could only be selectively forged by ring-closing alkyne metathesis (RCAM)/*trans* reduction using the latest generation of alkyne metathesis catalysts.

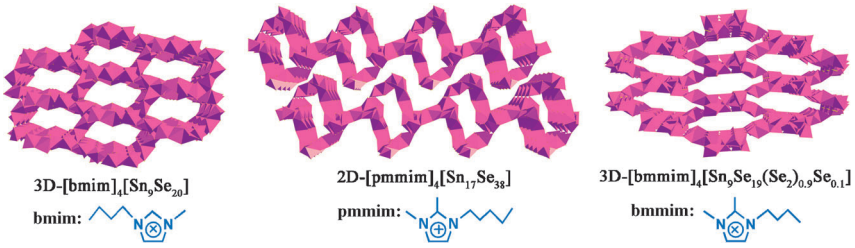
Natural Products

Contents

Enhanced control: Electrochemically mediated atom transfer radical polymerization (ATRP) allows easy modulation of the overall rate and control of polymerization through the variation of an external applied potential, E_{app} (see picture). This method has been successfully applied to aqueous ATRP of oligo(ethylene glycol) methyl ether methacrylate ($OEOMA_{475}$) catalyzed by Cu/tris(2-pyridylmethyl)-amine.



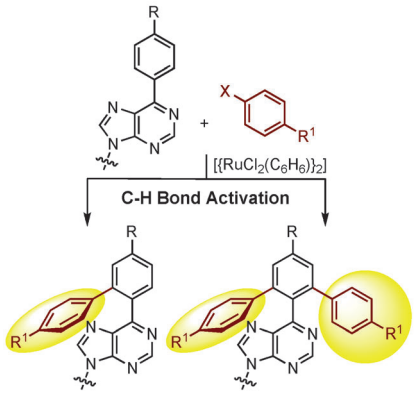
Atom Transfer Radical Polymerization



Ionic Liquids

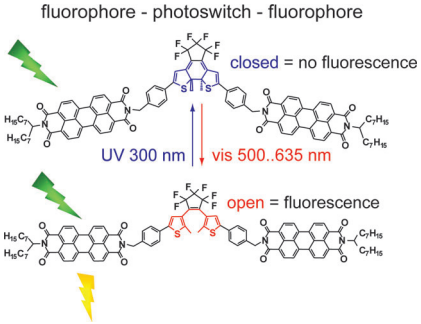
Ready to direct: Crystalline selenidostannates were synthesized in imidazolium-based ionic liquids with a small amount of hydrazine monohydrate as additive (see scheme). They are the first open-framework chalcogenides structurally directed by imidazolium cations and are inaccessible by traditional methods.

One aryl or two? The title reaction predominantly gives the monoarylation products with various amounts of diarylation product being observed in almost all cases (see scheme). Aryl iodides as well as aryl bromides were reactive under the optimized reaction conditions. The multiple nitrogen atoms in the purine, and oxygen atoms in the saccharide posed no problems in these transformations.



C–H Bond Activation

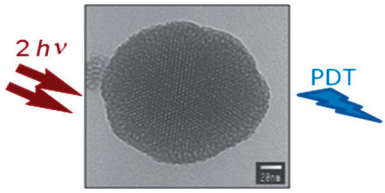
It takes three: The key functionalities of an optical transistor, gating and amplification, are demonstrated exploiting the photophysical properties of a molecular triad (see picture). Two building blocks of the triad are highly efficient fluorophores, whereas the third building block is a photochromic molecule that can be reversibly interconverted between two bistable forms by light.



Organic Optical Transistors

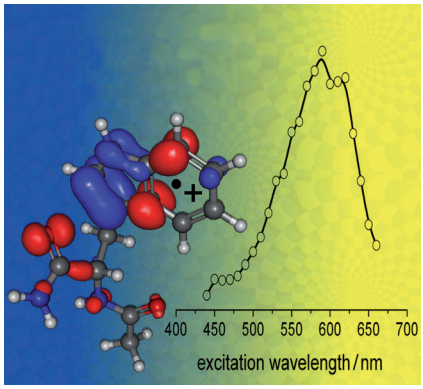
Contents

Zap 'em! Multifunctionalized mesoporous silica nanoparticles induce significant reduction of tumor size upon two-photon excitation in the near-infrared region while being nontoxic under daylight illumination. These nanoparticles were further tested for in vivo two-photon photodynamic therapy (TPE-PDT). A 70% regression of tumor size after a single treatment was observed in athymic mice bearing tumor xenografts.

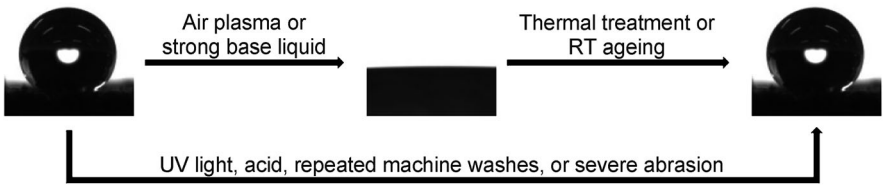


Photodynamic Therapy

Mellow yellow: The canonical form of the tryptophan radical cation embedded in an isolated polypeptide shows a distinctive absorption in the yellow region of the spectrum, in contrast with the neutral radical form, which shows an absorption in the blue region (see picture). The spectroscopic diagnostic was supported by vibrational spectroscopy (IRMPD), time-dependent density functional theory, and multireference perturbation theory.

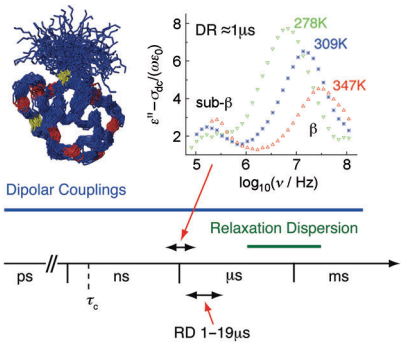


Protein Radicals



A fabric coating prepared from a homogeneous mixture of fluorinated-decyl polyhedral oligomeric silsesquioxane and hydrolyzed fluorinated alkyl silane shows remarkable self-healing superhydrophobic and superoleophobic properties and excellent durability against UV light, acid, repeated machine washes, and severe abrasion (see picture).

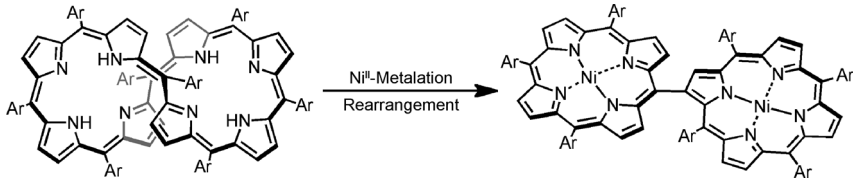
Fabric Coatings



A good combination: The lifetime of interconversion among the ground states of a protein ensemble representation could only be assigned to a time window that is four orders of magnitude large and ranges from 4 ns to 50 μs. By combining temperature-dependent NMR relaxation dispersion (RD) experiments and dielectric relaxation (DR) spectroscopy in solution, the lifetime was now identified to a value of (10 ± 9) μs at 309 K.

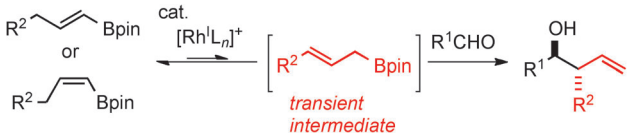
Protein Dynamics

Contents



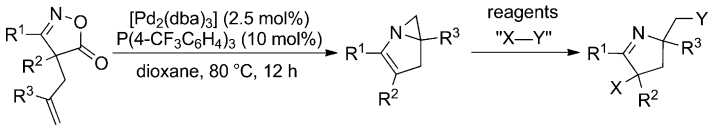
Breaking and entering: A figure-of-eight dinickel(II) complex and skeletal rearrangement products including a pyrrole-ring-cleaved product, a directly meso-β-linked diporphyrin (see scheme), and a dearylative oxygenation product have been formed in moderate yields by a nickel(II) metalation of [36]octaphyrin(1.1.1.1.1.1.1.1) in acetonitrile.

Porphyrinoids



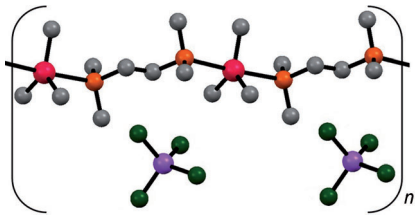
Synthetic equivalents: 1-Alkenylboronates perform the role of an allylating reagent. Their reaction with aldehydes in the presence of a cationic rhodium(I)/dppm catalyst results in a highly diastereoselective production of *anti*-configured homoallylic alcohols (see scheme; Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl).

Allylation Reactions



A decarboxylative intramolecular aziridination reaction of alkene-tethered 4*H*-isoxazol-5-ones with a palladium/phosphine catalyst gave 1-azabicyclo[3.1.0]hex-2-enes in moderate to high yields (see scheme; dba = dibenzylideneacetone). The resulting N-fused bicyclic aziridines readily reacted with various reagents to afford ring-opening pyrroline derivatives.

Synthetic Methods



Rare examples of P–Sn bonded cations (see structure; purple Al, gray C, green Cl, orange P, red Sn) are formed in reactions of Me_3P or $Me_2PCH_2CH_2PMe_2$ with Me_3SnCl or nBu_2SnCl_2 in the presence of a halide abstracting agent. The demonstrated versatility of the reactions, structures and bonding arrangements bodes well for the development of a diverse P–Sn chemistry by exploiting coordination chemistry for P–Sn bond formation.

Phosphorus–Tin Compounds

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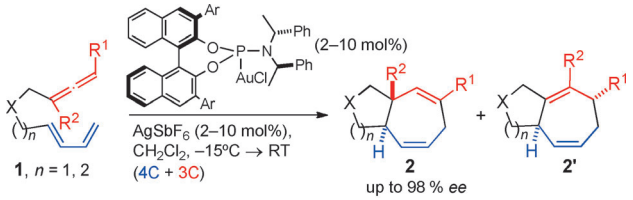
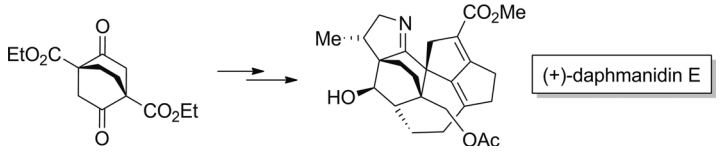


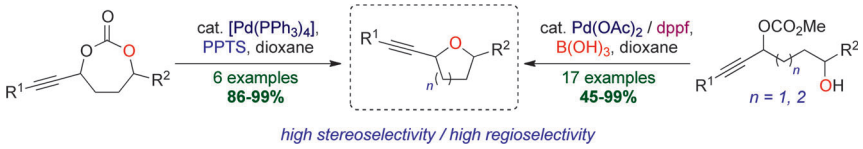
Allene-tethered dienes (**1**) undergo an intramolecular and highly enantioselective (4+3) cycloaddition when treated with suitable chiral phosphoramidite/gold(I) catalysts (see scheme; Ar = 9-anthracenyl). The reactions provide synthetically relevant [5.3.0] and [5.4.0] fused bicyclic systems **2** with good yields, complete diastereocontrol, and excellent enantioselectivities.

Enantioselective Cycloaddition



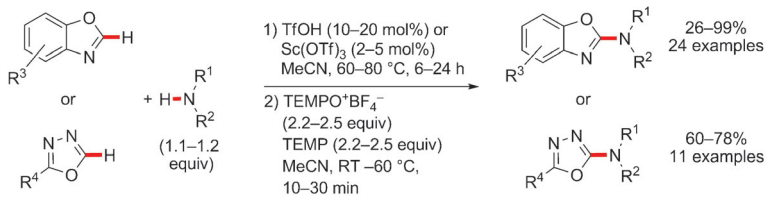
From ring to ring: The first total synthesis of (+)-daphmanidin E features rapid access to an enantiomerically pure bicyclo[2.2.2]octadione and elaboration around its periphery through the implementation of two Claisen rearrangements, the use of a copper/peptide complex for reagent-controlled stereoselective conjugate addition, a diastereoselective hydroboration, and a cobalt-catalyzed alkyl-Heck cyclization.

Natural Products



Oxyacetylene: Unusual palladium-catalyzed cyclizations of cyclic and acyclic propargylic carbonates give 2-alkynyl oxacycles. The reactions proceed with very high stereoselectivity for both *syn*- and *anti*-disubstituted furans and pyrans, and with exceptional regioselectivity. In addition, two-directional cyclizations of bispropargylic carbonate substrates yield bifurans with complete stereocontrol for all diastereomers.

Oxygen Heterocycles



No transition metals are necessary to convert benzoxazoles and 1,3,4-oxadiazoles into the corresponding pharmacologically interesting 2-aminated heterocycles by formal direct C(2)-amination using tetramethylpiperidine-*N*-oxoammonium tetrafluoroborate (TEMPO$^+$BF$_4^-$) as an oxidant (see scheme; TEMP = 2,2,6,6-tetramethylpiperidine; TfOH = trifluoromethanesulfonic acid).

C–H Amination

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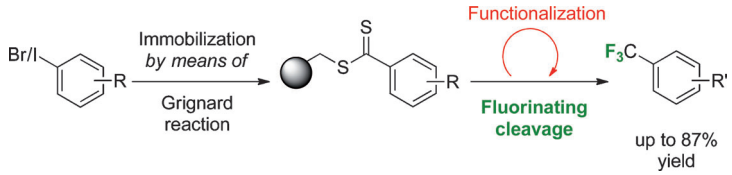
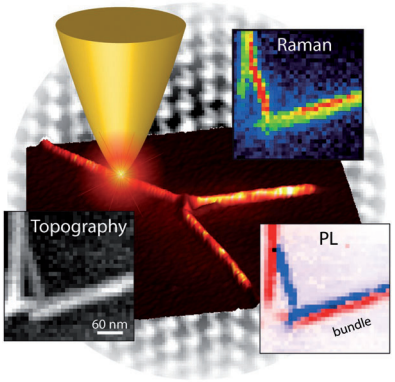


Save the best for last: In the first method for the trifluoromethylation of immobilized arenes, the aryl halides are attached through a dithioester linkage to the Merrifield resin and then functionalized by means of numerous reactions including transition-metal-catalyzed cross-couplings. In the final step the fluorinating cleavage reaction provides the trifluoromethylarenes in good yields and high purities.

Trifluoromethylation

Down to the wire: High-resolution photoluminescence (PL) and Raman images of CdSe nanowires were obtained using tip-enhanced near-field optical microscopy. They show that the optical properties of the CdSe nanowires vary significantly within a few nanometers leading to strong spatial fluctuations in both PL intensities and energies (see picture).



Nanomaterials

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Service