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:

*I. Bejan, D. Scheschkewitz**
Two Si=Si Bonds Connected by a Phenylene Bridge

H. Tsujita, Y. Ura, S. Matsuki, K. Wada, T.-a. Mitsudo, T. Kondo**
Regio- and Stereoselective Synthesis of Enamides and Dienamides by Ruthenium-Catalyzed Co-oligomerization of *N*-Vinylamides with Alkenes or Alkynes

A.-M. L. Fuller, D. A. Leigh, P. J. Lusby*
One Template, Multiple Rings: Controlled Iterative Addition of Macrocycles onto a Single Binding Site Rotaxane Thread

*H. Matsuzawa, Y. Miyake, Y. Nishibayashi**
Ruthenium-Catalyzed Enantioselective Propargylation of Aromatic Compounds with Propargylic Alcohols via Allenylidene Intermediates

*C. Fehr**
Catalytic, Enantioselective Tautomerization of Isolated Enols

*J. S. J. McCahill, G. C. Welch, D. W. Stephan**
Reactivity of Frustrated Lewis Pairs: Three Component Reactions of Phosphine, Borane, and Olefins

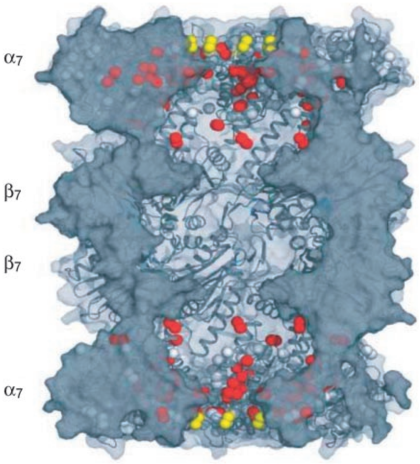
News

Books

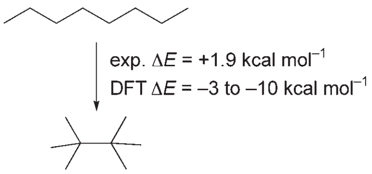
Highlights

NMR Spectroscopy

Bigger and bigger: A decade ago the size limit for biomolecular NMR spectroscopy was thought to be on the order of 30 kDa. Now quantitative NMR-relaxation studies have been reported for a 670-kDa complex (see structure; red: Me groups with slow dynamics, yellow: Me groups at highly flexible N termini). The key developments that led to the remarkable work are presented.



Density Functional Theory



Not so simple: Common and broadly used density functional theory (DFT) implementations do not properly account for medium-range electron correlation. The resultant errors in energy calculations, for example, for simple hydrocarbon isomers, can be large and increase with increasingly larger structures.

Contents

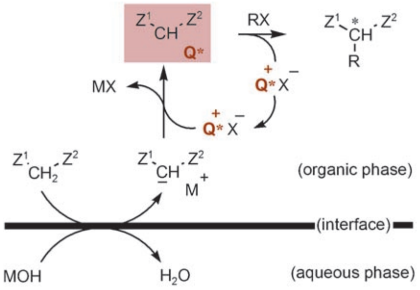
Reviews

Asymmetric Synthesis

T. Ooi, K. Maruoka* ——— **4222 – 4266**

Recent Advances in Asymmetric Phase-Transfer Catalysis

Chiral ion pair lends a hand: Asymmetric phase-transfer catalysis, as represented by chiral quaternary onium salts, has become an increasingly important method for the synthesis of optically active organic molecules. The multiple ion-exchange process catalytically generates a chiral ion pair, whose chiral onium cation creates an effective asymmetric environment around the nucleophilic anion and enables stereoselective bond formation (see scheme).



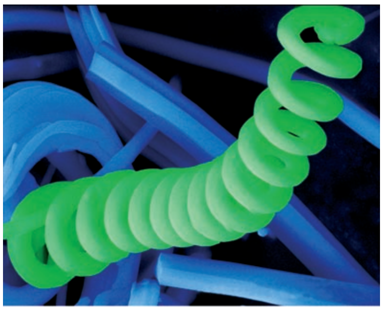
Communications

Supramolecular Architecture

C. Arnal-Hérault, A. Banu, M. Barboiu,* M. Michau, A. van der Lee — **4268 – 4272**

Amplification and Transcription of the Dynamic Supramolecular Chirality of the Guanine Quadruplex

Transcribing twists: A new way to transcribe the supramolecular chirality of a dynamic G-quadruplex supramolecular architecture (G: guanine) is reported, thereby creating hybrid twisted nanorods or inorganic microsprings (see image). The first picture of a dynamic G-quadruplex transcribed at the nanometric level is reported.

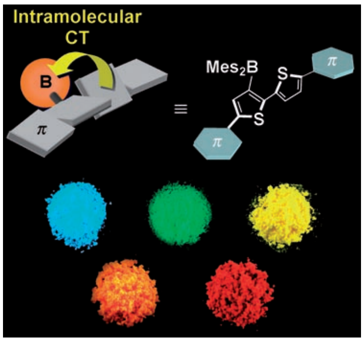


Emissive Organic Solids

A. Wakamiya, K. Mori, S. Yamaguchi* ——— **4273 – 4276**

3-Boryl-2,2′-bithiophene as a Versatile Core Skeleton for Full-Color Highly Emissive Organic Solids

Seeing the light: Tuning the electron-donating ability of the π-conjugated framework of bithiophene has resulted in intense solid-state emissions with maxima ranging over a wide visible region (see picture). Even a deep-red fluorescence with a large Stokes shift close to 200 nm, arising from the intramolecular charge-transfer (CT) transition from the twisted bithiophene π framework to the boron center, can be obtained.



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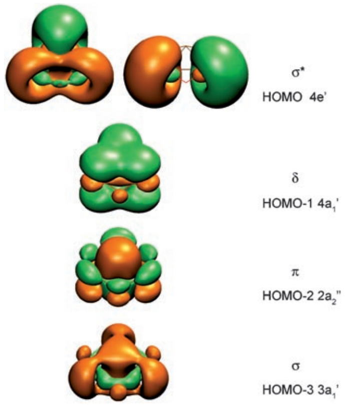
Aromaticity

H. J. Zhai, B. B. Averkiev, D. Y. Zubarev, L. S. Wang,* A. I. Boldyrev* **4277 – 4280**

δ Aromaticity in $[Ta_3O_3]^-$

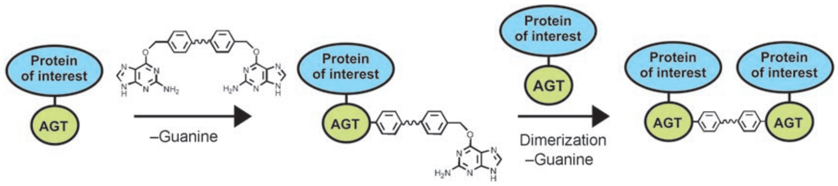


Low-lying electronic transitions are observed in the photoelectron spectra of $[Ta_3O_3]^-$, and ab initio calculations show that the cluster has a planar D_{3h} triangular structure. Totally delocalized, multicenter metal–metal bonding renders δ aromaticity for $[Ta_3O_3]^-$ (see picture). This is the first δ-aromatic molecule to be confirmed both experimentally and theoretically.

Protein–Protein Interactions

G. Lemercier, S. Gendreizig, M. Kindermann, K. Johnsson* **4281 – 4284**

Inducing and Sensing Protein–Protein Interactions in Living Cells by Selective Cross-linking

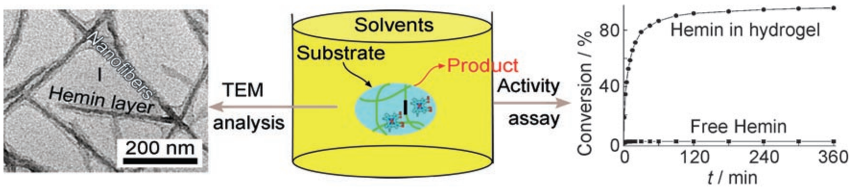


Cells technique: Small molecules have been synthesized that enable the covalent and irreversible dimerization of fusion proteins of O^6-alkylguanine-DNA alkyltransferase (AGT or SNAP-Tag) in vitro and in living cells. The cross-linking efficiency of AGT fusion proteins provides a measure to characterize the proximity and interactions of protein pairs in living cells (see scheme).

Enzyme Mimetics

Q. Wang, Z. Yang, X. Zhang, X. Xiao, C. K. Chang,* B. Xu* **4285 – 4289**

A Supramolecular-Hydrogel-Encapsulated Hemin as an Artificial Enzyme to Mimic Peroxidase



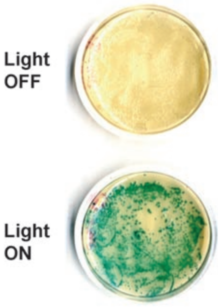
Faking it: The use of a supramolecular hydrogel as the structural component of artificial enzymes provides a new and useful approach to the development of biomimetic catalysts. In toluene, hemin chloride encapsulated in such a hydrogel achieves about 60% nascent catalytic activity of horseradish peroxidase. Additionally, the activity of hemin in the hydrogel is 387.1 times greater than that of free hemin.

Photochemical Gene Control

D. D. Young, A. Deiters* **4290 – 4292**

Photochemical Activation of Protein Expression in Bacterial Cells

Turning genes on with light: Photochemical control of gene expression is a versatile tool for the elucidation of biological processes and the programming of new biological functions. Activation of protein expression in prokaryotic cells through light irradiation is achieved through a photocaged small molecule. Spatiotemporal regulation of the *lac* operon was obtained through the application of a photocaged isopropyl-β-D-thiogalactopyranoside derivative.



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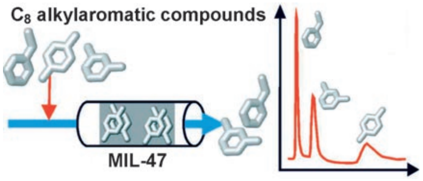
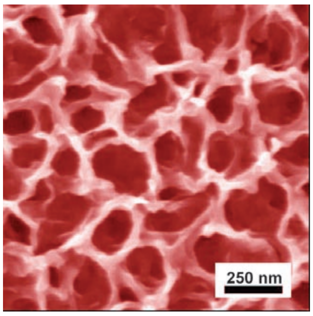


A breakthrough result: The microporous metal–organic framework MIL-47 is an excellent adsorbent for the separation of C_8 alkylaromatic compounds, such as ethylbenzene, *meta*-xylene, and *para*-xylene. The potential of MIL-47, with its high uptake capacity and its hydrophobic nature, for real separations of the C_8 alkylaromatic compounds was demonstrated by breakthrough and chromatographic experiments (see picture).

Metal–Organic Frameworks

L. Alaerts, C. E. A. Kirschhock, M. Maes, M. A. van der Veen, V. Finsy, A. Depla, J. A. Martens, G. V. Baron, P. A. Jacobs, J. F. M. Denayer, D. E. De Vos* **4293–4297**

Selective Adsorption and Separation of Xylene Isomers and Ethylbenzene with the Microporous Vanadium(IV) Terephthalate MIL-47



Sensitive sponges: Nanosponge titania (NST), integrated into a prototype device, has been used for ultrasensitive detection of hydrogen. NST has potential applications in multiplex sensing systems such as electronic noses and tongues, and three-dimensionally interconnected nanostructured metal oxides hold great promise as platforms for ultrasensitive sensors. The picture shows an SEM image of NST formed from 500-nm-thick Ti film.

Nanostructured Materials

A. S. Zuruzi,* N. C. MacDonald, M. Moskovits, A. Kolmakov **4298–4301**

Metal Oxide “Nanosponges” as Chemical Sensors: Highly Sensitive Detection of Hydrogen with Nanosponge Titania

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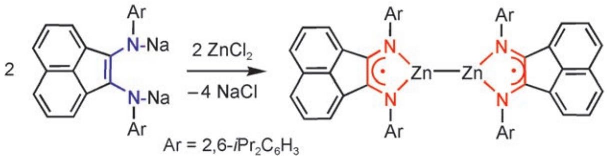

Radical help: The use of a spin-labeled ligand allows a zinc–zinc-bonded compound supported by radical-anionic ligands to be prepared (see scheme). The radical anion enabled the presence of the Zn—Zn bond in solution to be confirmed by ESR spectroscopy. DFT calculations confirm the biradical nature of the compound and indicate that the Zn—Zn bond is formed mainly by the metal s orbitals.

Biradicals

I. L. Fedushkin,* A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov, G. K. Fukin **4302–4305**

[(dpp-bian)Zn—Zn(dpp-bian)]: A Zinc–Zinc-Bonded Compound Supported by Radical-Anionic Ligands

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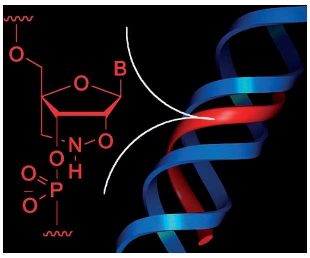
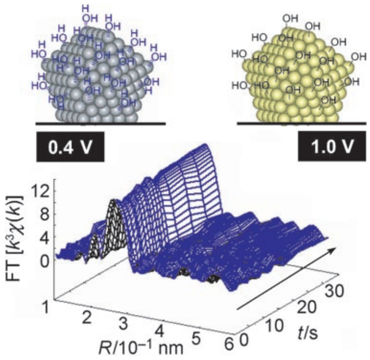
Good things come in threes: A novel bridged nucleic acid in which the furanose conformation was locked in the N form by a six-membered bridged moiety containing an N—O bond (see picture) has been developed. Triplex-forming oligonucleotides composed of this residue formed highly stable triplexes at physiological pH values.



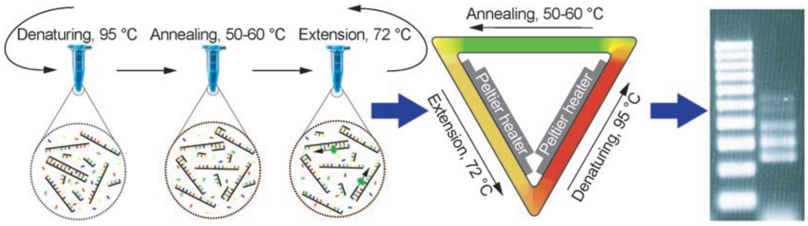
Bridged Nucleic Acids

S. M. A. Rahman, S. Seki, S. Obika, S. Haitani, K. Miyashita, T. Imanishi* **4306–4309**

Highly Stable Pyrimidine-Motif Triplex Formation at Physiological pH Values by a Bridged Nucleic Acid Analogue

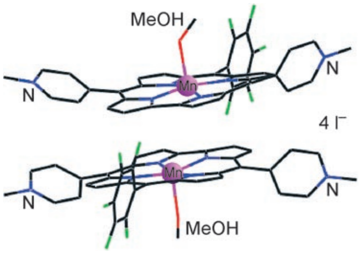


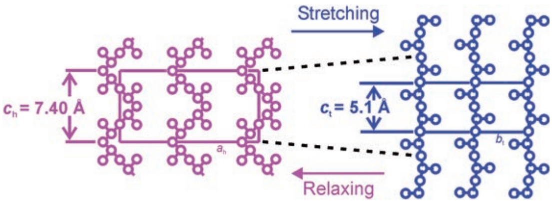
On the Pt/C cathode in a fuel cell, dynamic surface events were investigated by novel X-ray absorption techniques (see Fourier transform for the oxidation process, 0.4→1.0 V). Evidence for Pt dissolution at the cathode was found, and the reaction kinetics of the electron-transfer processes, as well as redox structural changes and a significant time lag between the events, were observed for the first time under operando conditions.



Is that a PCR in your pocket? An innovative thermocycling system is presented that harnesses natural convection to perform rapid multiplex and long-target DNA amplification by the polymerase chain reaction (PCR). The design is inherently simple and consumes minimal electrical power, enabling a pocket-sized battery-powered device to be constructed at a cost of approximately US$10.

DNA likes corroles and peroxynitrite doesn't: The water-soluble manganese corrole (crystal structure shown) is a much better catalyst than the analogous porphyrin for decomposition of peroxynitrite (HOONO). The interactions of the two complexes with DNA are also significantly different. These findings suggest that positively charged corroles may be useful for therapeutic approaches.





Under stress: A high level of crystallinity in polymers does not impair ductility and elastic performance if a stress-induced martensitic crystal–crystal phase transition takes place (see picture; c: unit cell axis, h: helical form, t: *trans*-planar form). This type of elasticity is not merely entropic but also partly enthalpic, and therefore similar to the superelasticity of shape-memory alloys.

Heterogeneous Catalysis

C. Ó Dálaigh, S. A. Corr, Y. Gun'ko,* S. J. Connon* ——— **4329–4332**

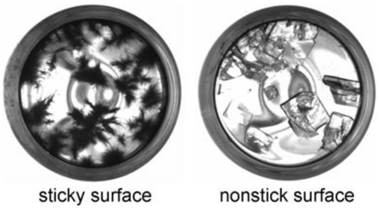
A Magnetic-Nanoparticle-Supported 4-*N*,*N*-Dialkylaminopyridine Catalyst: Excellent Reactivity Combined with Facile Catalyst Recovery and Recyclability

Quick recovery: The first magnetic-nanoparticle-supported organocatalyst is prepared. The heterogeneous catalyst promotes a range of nucleophilic reactions and can be recovered by exposure to an external magnet (see picture). Furthermore, it can be recycled over 30 times without loss of activity.

Polymorphism

J. R. Cox, L. A. Ferris, V. R. Thalladi* ——— **4333–4336**

Selective Growth of a Stable Drug Polymorph by Suppressing the Nucleation of Corresponding Metastable Polymorphs

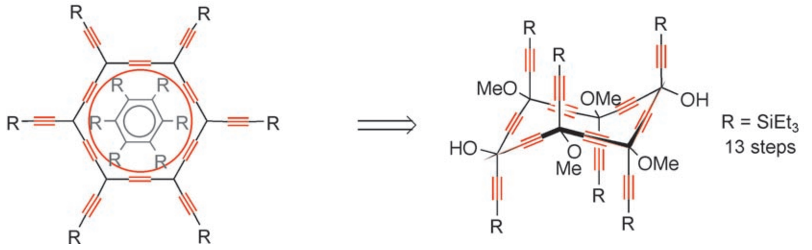


To stick or not to stick? Metastable (α) and stable (γ) polymorphs of indomethacin crystallize concomitantly from ethanol solutions. Crystallization in glass vials functionalized with perfluoroalkyl-terminated silane monolayers, however, leads to the exclusive growth of the stable polymorph. These monolayers create surfaces that inhibit the heterogeneous nucleation of α polymorph and thereby promote the growth of γ polymorph.

Aromatization

C. Zou, C. Duhayon, V. Maraval, R. Chauvin* ——— **4337–4341**

Hexasilylated Total Carbomer of Benzene

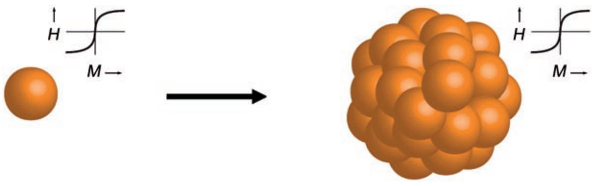


A close cousin of benzene: The cobalt-assisted reductive aromatization of a hexaalkynyl [6]pericyclyne afforded a fully expanded carbobenzene derivative (see scheme) as the first carbomer without stabilizing aromatic substituents. The triethylsilyl groups ensured high solubility and allowed full spectroscopic characterization of the aromatic macrocycle.

Nanostructures

J. Ge, Y. Hu, M. Biasini, W. P. Beyermann, Y. Yin* ——— **4342–4345**

Superparamagnetic Magnetite Colloidal Nanocrystal Clusters



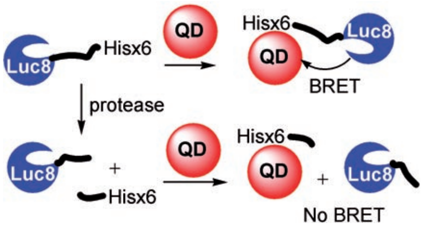
High-temperature hydrolysis of $FeCl_3$ in the presence of a surfactant gives monodisperse superparamagnetic colloidal nanocrystal clusters (CNCs) of magnetite with tunable sizes (30–180 nm; see scheme). The combination of superparamagnetism, high magnetization, and high water dispersibility makes these CNCs ideal candidates for applications such as drug delivery and bioseparation.

Contents

Nanosensors

H. Yao, Y. Zhang, F. Xiao, Z. Xia,
J. Rao* **4346–4349**

Quantum Dot/Bioluminescence Resonance Energy Transfer Based Highly Sensitive Detection of Proteases



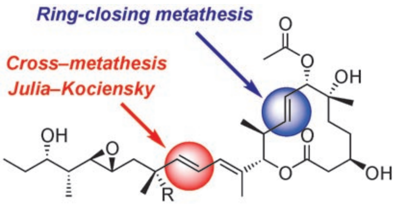
Sensing by BRET: Quantum dot (QD) nanosensors can detect the activity of matrix metalloproteinases by measuring the bioluminescence resonance energy transfer (BRET) efficiency between the QDs and a bioluminescent fusion protein (see scheme; Luc8 = *Renilla* luciferase; His × 6 = six-histidine tag).

Total Synthesis

R. M. Kanada, D. Itoh, M. Nagai,
J. Niijima, N. Asai, Y. Mizui, S. Abe,
Y. Kotake* **4350–4355**

Total Synthesis of the Potent Antitumor Macrolides Pladienolide B and D

Getting cross: The total syntheses of two pladienolides (see picture), which have prominent antitumor activity based on a unique mechanism of action, have been accomplished, and their absolute configurations were verified. The 12-membered aliphatic macrolide structure was formed by ring-closing metathesis, and the side-chain moiety was coupled to the macrolide by Julia–Kocienski olefination or cross-metathesis.

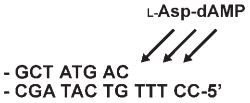


Pladienolide B: R = H
D: R = OH

Amino Acids

O. Adelfinskaya,
P. Herdewijn* **4356–4358**

Amino Acid Phosphoramidate Nucleotides as Alternative Substrates for HIV-1 Reverse Transcriptase



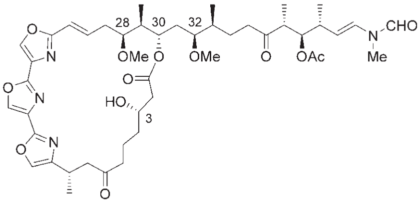
Pick and choose: Amino acid phosphoramidites, in particular Asp-dAMP (dAMP = 2′-deoxyadenosine-5′-monophosphate) and His-dAMP, act in a template-dependent DNA synthesis assay as alternative substrates for reverse transcriptase. L-Aspartic acid can function as a leaving group during DNA synthesis and can be considered as a pyrophosphate mimetic in this reaction.

Macrolide Synthesis

G. Pattenden,* N. J. Ashweek,
C. A. G. Baker-Glenn, G. M. Walker,
J. G. K. Yee **4359–4363**

Total Synthesis of (−)-Ulapualide A: The Danger of Overdependence on NMR Spectroscopy in Assignment of Stereochemistry

Lessons learnt: The asymmetric total synthesis of the macrolide (−)-ulapualide A has been accomplished. Interestingly, the ^{1}H NMR spectrum and chiroptical data of the macrolide and of a previously synthesized diastereoisomer with opposite stereocenters at C3, C28, C29, C30, and C32 were superimposable, which highlights the care that must be taken in the assignment of configurations to complex structures based on NMR spectroscopy.

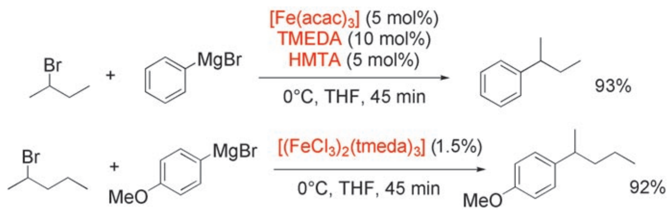


(−)-ulapualide A

Homogeneous Catalysis

G. Cahiez,* V. Habiak, C. Duplais,
A. Moyeux ______ **4364 – 4366**

Iron-Catalyzed Alkylations of Aromatic Grignard Reagents

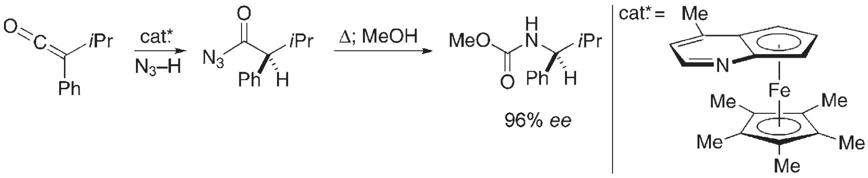


Any old iron: Two efficient iron-catalyzed cross-coupling reactions between aryl Grignard reagents and alkyl bromides were developed that are suitable for large-scale applications. The first procedure uses iron acetylacetonate and involves a cooperative effect between the two ligands *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and hexamethylenetetraamine (HMTA), while the second procedure uses $[(FeCl_3)_2(tmeda)_3]$ as catalyst.

Asymmetric Catalysis

X. Dai, T. Nakai, J. A. C. Romero,
G. C. Fu* ______ **4367 – 4369**

Enantioselective Synthesis of Protected Amines by the Catalytic Asymmetric Addition of Hydrazoic Acid to Ketenes

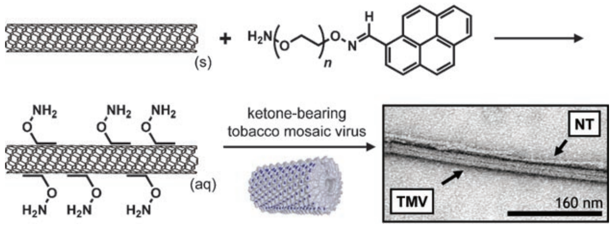


A-mine of possibilities: An effective method for the conversion of achiral ketenes into enantioenriched protected amines was developed by tuning the structure and reactivity of a catalyst on the basis of a mechanistic hypothesis. The method involved the catalytic asymmetric addition of hydrazoic acid to ketenes, followed by a Curtius rearrangement (see scheme).

Nanotubes

P. G. Holder, M. B. Francis* **4370 – 4373**

Integration of a Self-Assembling Protein Scaffold with Water-Soluble Single-Walled Carbon Nanotubes

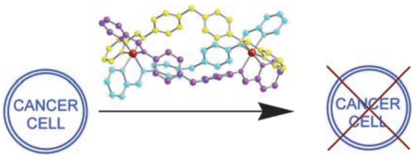


Plastic tubing: The parallel alignment of single-walled carbon nanotubes (NTs) with a self-assembling biomolecular scaffold, the tobacco mosaic virus (TMV), is presented. A multifunctional polymeric surfactant brings together these two disparate components: The NTs are solubilized by a layer of poly(ethylene glycol) attached through a pyrene anchor, and the pendant alkoxyamine groups of the surfactant allow mild bioconjugation with ketone-labeled proteins.

Anticancer Agents

G. I. Pascu, A. C. G. Hotze,
C. Sanchez-Cano, B. M. Kariuki,
M. J. Hannon* ______ **4374 – 4378**

Dinuclear Ruthenium(II) Triple-Stranded Helicates: Luminescent Supramolecular Cylinders That Bind and Coil DNA and Exhibit Activity against Cancer Cell Lines



A fluorescent supramolecular cylinder binds noncovalently to DNA and shows anticancer activity in cell lines.

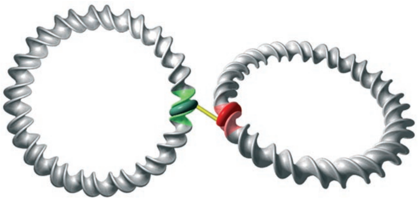
Contents

Synthetic Methods

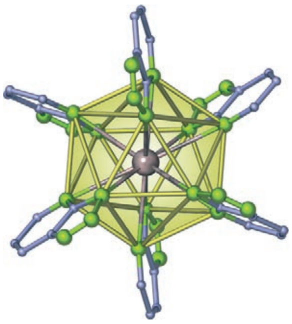
Axial-to-central chirality transfer is highly efficient in a regioselective synthesis of (1-sulfonyl)alkylidenethiiranes from 1,2-allenyl sulfones (see scheme). A cyclic intermediate formed upon the electrophilic addition of bromine to the allene was isolated and characterized. A mechanism is proposed on the basis of this intermediate and the observed stereoselectivity.

DNA Conjugation

Copy and paste: A DNA strut consisting of two Dervan polyamides is constructed with two sides that can sequence-selectively bind double-stranded DNA. This strut can be used as sequence-selective glue for DNA architectures and can easily combine DNA objects that are 100 times its mass.



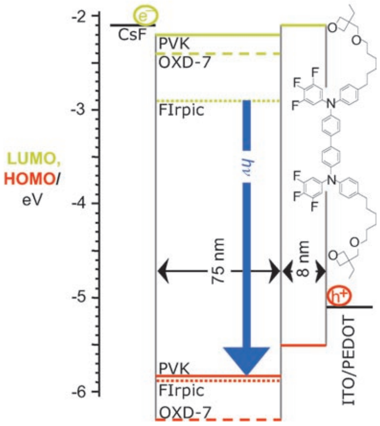
Metal–Organic Frameworks

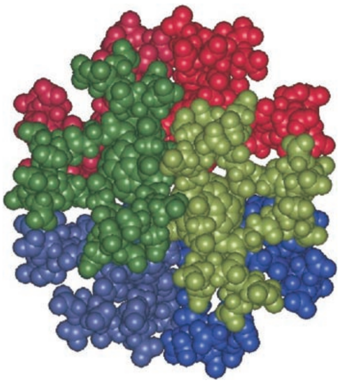


Eu assembly: The reaction of europium with 1*H*-1,2,3-triazolo[4,5-*b*]pyridine under solvothermal conditions in pyridine gives $^{3}_{\infty}$[Eu(Tzpy)$_2$]. This novel homoleptic framework contains Eu^{II} centers that are icosahedrally coordinated by the 12 nitrogen atoms of six chelating ligands (see picture; Eu bronze, C blue, N green).

Blue Light-Emitting Diodes

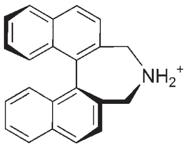
Shedding a blue light: A series of oxetane-functionalized crosslinkable triphenylamine dimers (XTPDs) is investigated as the hole-transport layers in blue-phosphorescent polymer light-emitting diodes (see scheme). These devices have improved performance characteristics, and their luminous efficiencies depend on the HOMO energies of the XTPDs.



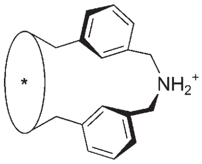


Six molecules of an amphiphilic fullerene derivative make up the smallest persistent micelle detected so far (see picture, the six amphiphilic molecules are shown in different colors). These micelles can be used to systematically study the factors that determine the structural persistence of micelles and may lead to the design of tailor-made supramolecular containers.

Micelles



(*P*)-**1**



(*P*)-**2**

The trick with the chiral clamp: In metacyclophanes such as (*P*)-**2** it is possible to stabilize one chiral conformation by means of a chiral clamp so effectively that at room temperature only this conformation is present. This conformation resembles that of *o*,*o*′-bridged binaphthyls (for example (*P*)-**1**). New binaphthyl alternatives are thus made accessible.

Chirality

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service