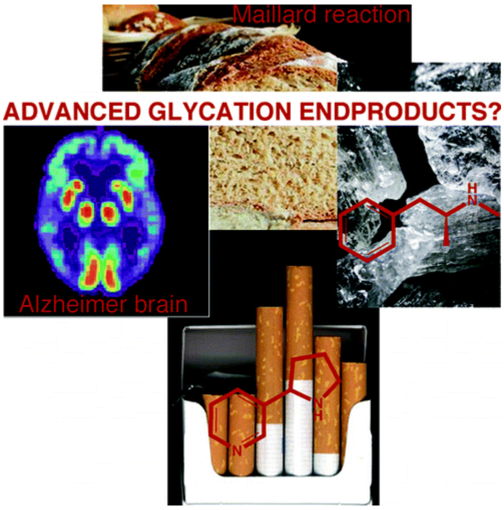
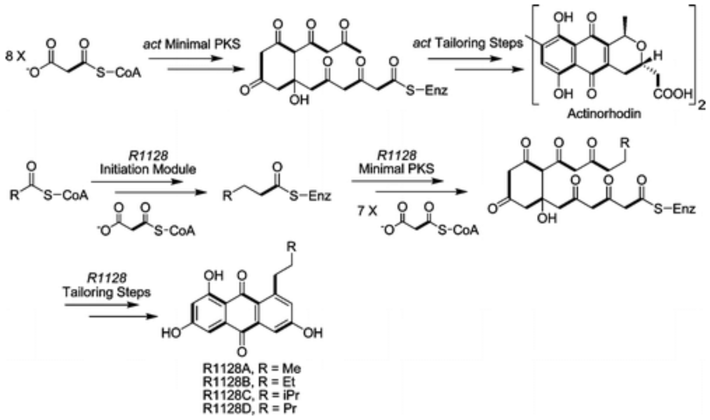
- Drugs of Abuse That Mediate Advanced Glycation End Product Formation: A Chemical Link to Disease Pathology
  Treweek, J. B.; Dickerson, T. J.; Janda, K. D. *Acc. Chem. Res.* **2009**, *42*, 659–669.
  Abstract:



Nicotine and methamphetamine are frequently abused in modern society, despite the increasing evidence of their addictive, neuropharmacological, and toxic effects. Tobacco, the most widely abused substance, is the leading cause of preventable death in the United States, killing nearly half a million Americans annually. A methamphetamine epidemic has also spread during the past decade; severe neurotoxicity and addictiveness contribute to the drug's notoriety. Although the majority of research on these two drugs is of pharmacological and neurobiological motivation, further study of these molecules from a chemical perspective may provide novel mechanistic insight into either their addictive potential or their pathological effects. For example, nicotine and methamphetamine share a common structural feature, a secondary amine, suggesting that these molecules could possess similar (or analogous) *in vivo* reactivity. Discoveries concerning the synthetic requirements for aqueous aldol catalysis and the feasibility of the enamine mechanism under physiological conditions have given rise to the hypothesis that ingested molecules, such as abused drugs, could participate in reactions utilizing an enamine intermediate *in vivo.*

The chemical reactivity of exogenous drugs with amine functionalities was initially examined in the context of the Maillard reaction, or nonenzymatic browning. The heating of reducing sugars with amino acids yields a brown solution; studies of this reaction were originally applied to food chemistry for the production of distinct flavors and aromas. Further research has since revealed numerous instances in which the *in vivo* production of advanced glycation end products (AGEs) through the Maillard reaction contribute to the pathology of disease states. Specifically, the modification of long-lived proteins by glycation and glycoxidation and the accumulation of these AGEs compromise the original function of such proteins and change the mechanical properties of affected tissue. In this Account, we summarize our investigations into the capacity for exogenous compounds to initiate the Maillard reaction and the corresponding physiological and immunological impact of the drug-conjugated AGEs that form. Many of the pathological components of diabetes, atherosclerosis, cancer, macular degeneration, Alzheimer's disease, and even the normal aging process are attributable to AGEs and their potential for aggregate formation in the vasculature. A deeper understanding of AGEs, and particularly glycated proteins, will provide fundamental mechanistic insight into disease origins.

- Biosynthesis of Aromatic Polyketides in Bacteria
  Das, A.; Khosla, C. *Acc. Chem. Res.* **2009**, *42*, 631–639.
  <u>Abstract:</u>



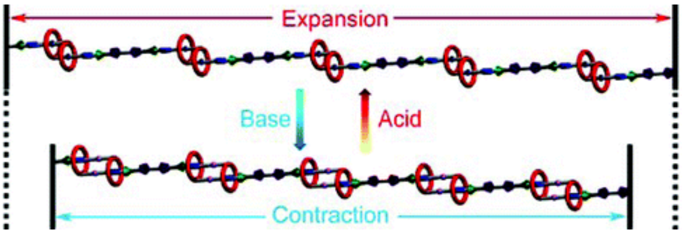
Natural products, produced chiefly by microorganisms and plants, can be large and structurally complex molecules. These molecules are manufactured by cellular assembly lines, in which enzymes construct the molecules in a stepwise fashion. The means by which enzymes interact and work together in a modular fashion to create diverse structural features has been an active area of research; the work has provided insight into the fine details of biosynthesis.

A number of polycyclic aromatic natural products – including several noteworthy anticancer, antibacterial, antifungal, antiviral, antiparasitic, and other medicinally significant substances – are synthesized by polyketide synthases (PKSs) in soil-borne bacteria called actinomycetes. Concerted biosynthetic, enzymological, and structural biological investigations into these modular enzyme systems have yielded interesting mechanistic insights. A core module called the minimal PKS is responsible for synthesizing a highly reactive, protein-bound poly-*β*-ketothioester chain. In the absence of other enzymes, the minimal PKS also catalyzes chain initiation and release, yielding an assortment of polycyclic aromatic compounds. In the presence of an initiation PKS module, polyketide backbones bearing additional alkyl, alkenyl, or aryl primer units are synthesized, whereas a range of auxiliary PKS enzymes and tailoring enzymes convert the product of the minimal PKS into the final natural product.

In this Account, we summarize the knowledge that has been gained regarding this family of PKSs through recent investigations into the biosynthetic pathways of two natural products, actinorhodin and R1128 (A-D).

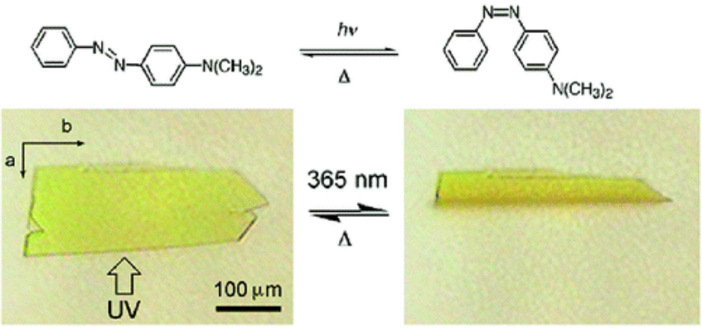
We also discuss the practical relevance of these fundamental insights for the engineered biosynthesis of new polycyclic aromatic compounds. With a deeper understanding of the biosynthetic process in hand, we can assert control at various stages of molecular construction and thus introduce unnatural functional groups in the process. The metabolic engineer affords a number of new avenues for creating novel molecular structures that will likely have properties akin to their fully natural cousins.

- Acid−Base Actuation of [c2]Daisy Chains
  Fang, L.; Hmadeh, M.; Wu, J.; Olson, M. A.; Spruell, J. M.; Trabolsi, A.; Yang, Y. W.; Elhabiri, M.; Albrecht-Gary, A. M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 7126–7134.
  <u>Abstract:</u>



A versatile synthetic strategy, which was conceived and employed to prepare doubly threaded, bistable [c2]daisy chain compounds, is described. Propargyl and 1-pentenyl groups have been grafted onto the stoppers of [c2]daisy chain molecules obtained using a template-directed synthetic protocol. Such [c2]daisy chain molecules undergo reversible extension and contraction upon treatment with acid and base, respectively. The dialkyne-functionalized [c2]daisy chain (AA) was subjected to an [AA+BB] type polymerization with an appropriate diazide (BB) to afford a linear, mechanically interlocked, main-chain polymer. The macromolecular properties of this polymer were characterized by chronocoulometry, size exclusion chromatography, and static light-scattering analysis. The acid−base switching properties of both the monomers and the polymer have been studied in solution, using 1H NMR spectroscopy, UV/vis absorption spectroscopy, and cyclic voltammetry. The experimental results demonstrate that the functionalized [c2]daisy chains, along with their polymeric derivatives, undergo quantitative, efficient, and fully reversible switching processes in solution. Kinetics measurements demonstrate that the acid/base-promoted extension/contraction movements of the polymeric [c2]daisy chain are actually faster than those of its monomeric counterpart. These observations open the door to correlated molecular motions and to changes in material properties.

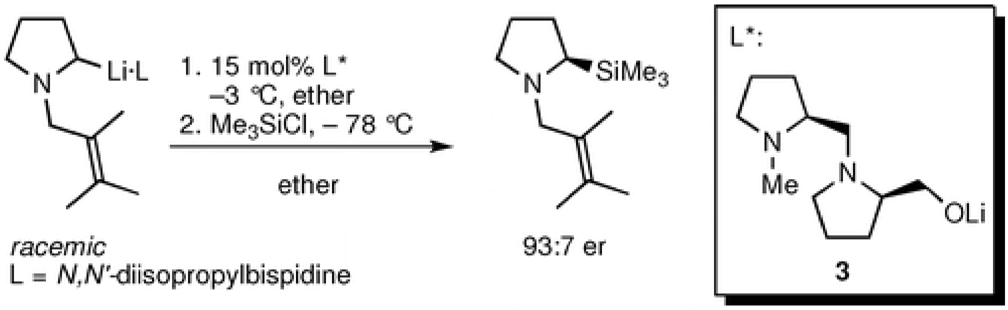
- Mechanical Motion of Azobenzene Crystals upon Photoirradiation
  Koshima,H.; Ojima, N.; Uchimoto, H. *J. Am. Chem. Soc.* **2009**, *131*, 6890–6891.
  <u>Abstract:</u>



Photomechanical bending of trans-4-(dimethylamino)azobenzene microcrystals was observed. Upon UV irradiation, the (001) face of the platelike microcrystals bent quickly in the direction opposite the light source, reaching the maximum deflection after 0.5 s. The microcrystal returned to its initial flat shape 30 s after the illumination was stopped. This mechanical motion was reversible over repeated cycles of UV irradiation. The bending effect was attributed to a gradient in the extent of UV-induced trans−cis photoisomerization as a function of light penetration, causing the expansion of the irradiated crystal surface along the b axis to result in a bent macrostructure.

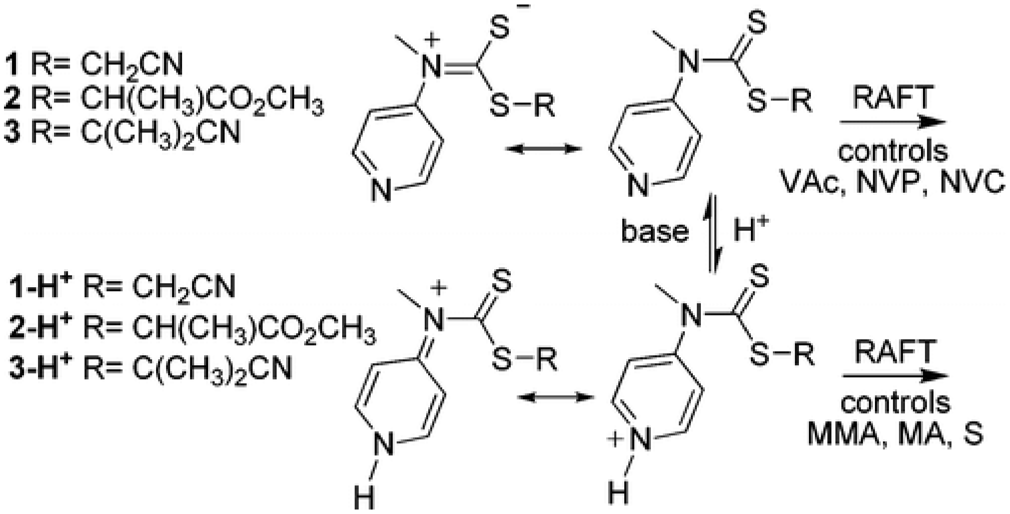
- Enantiomerization Dynamics and a Catalytic Dynamic Resolution of *N*-Trimethylallyl-2-lithiopyrrolidine
  Beng, T. K.; Yousaf, T. I.; Coldham, I.; Gawley, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 6908–6909.

Abstract:



The barriers to enantiomerization of *N*-trimethylallyl-2-lithiopyrrolidine have been measured in the presence of sparteine,**1**, *N*,*N*-diisopropylbispidine, **2**, and diaminoalkoxide **3**. We have additionally demonstrated a rare example of a catalytic dynamic resolution using either of two ligands, achieving enantiomer ratios of up to 93:7.

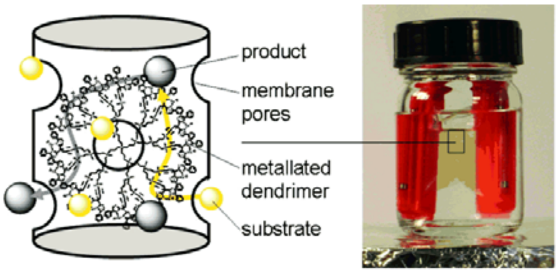
- Universal (Switchable) RAFT Agents
  Benaglia, M.; Chiefari, J.; Chong, Y. K.; Moad, G.; Rizzardo, E.; Thang, S. H. *J. Am. Chem. Soc.* **2009**, *131*, 6914–6915.
  Abstract:



The polymerization of most monomers that are polymerizable by radical polymerization can be controlled by the reversible addition−fragmentation chain transfer (RAFT) process. However, it is usually required that the RAFT agent be selected according to the types of monomer being polymerized. Thus, RAFT agents (dithioesters, trithiocarbonates) suitable for controlling polymerization of "more activated" monomers (MAMs; e.g., styrene, acrylates, methacrylates, etc.) tend to inhibit polymerization of "less activated" monomers (LAMs; e.g., vinyl acetate, *N*-vinylpyrrolidone, etc.). Similarly RAFT agents suitable for polymerizations of LAMs (xanthates, certain dithiocarbamates) tend to give little or poor control over polymerizations of MAMs. We now report a new class of "switchable" RAFT agents, *N*-(4-pyridinyl)-*N*-methyldithiocarbamates, that provide excellent control over polymerization of LAMs and, after addition of 1 equiv of a protic or Lewis acid, become effective in controlling polymerization of MAMs, allowing the synthesis of poly(MAM)-*block*-poly(LAM) with narrow molecular weight distributions.

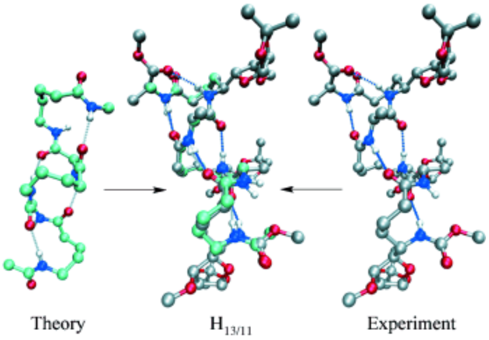
- "Catalysis in a Tea Bag": Synthesis, Catalytic Performance and Recycling of Dendrimer-Immobilised Bis- and Trisoxazoline Copper Catalysts

Gaab, M.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Eur. J.* **2009***, 15*, 5450-5462.
Abstract:



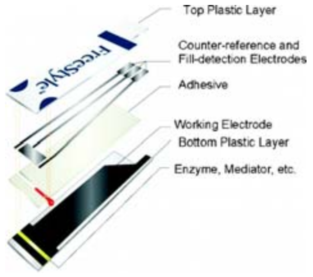
Trapped in a "tea bag": Membrane bags, fabricated from a dialysis membrane, have been employed as semipermeable containers for dendrimer-immobilised oxazoline-copper(II) Lewis acid catalysts. Dipping them into reactant solutions leads to the catalytic conversion of the substrates, which penetrate the membrane as does the product in the reverse direction (see scheme).
Bis- and trisoxazolines (BOX and trisox), containing a linker unit in the ligand backbone that allows their covalent attachment to carbosilane dendrimers, have been employed as polyfunctional ligands for recyclable Cu^{II} Lewis acid catalysts that were immobilised in a membrane bag. The oxazolines contained an alkynyl unit attached to their backbone that was deprotonated with LDA or BuLi and then reacted with the chlorosilyl termini of zeroth-, first- and second-generation carbosilane dendrimers in the presence of $TlPF_6$. The functionalised dendritic systems were subsequently separated from excess ligand by way of dialysis. The general catalytic potential of these systems was assessed by studying two benchmark reactions, the α-hydrazination of a β-keto ester as well as the Henry reaction of 2-nitrobenzaldehyde with nitromethane. For both reactions the bisoxazoline-based catalysts displayed superior selectivity and, in particular, catalyst activity. The latter was interpreted as being due to the hindered decoordination of the third oxazoline unit, the key step in the generation of the active catalyst, in the immobilised trisox-copper complexes. Solutions of the second-generation dendrimer catalysts were placed in membrane bags, fabricated from commercially available dialysis membranes, with the purpose of catalyst recycling based on dialysis. Overall, the supported BOX catalyst gave good and highly reproducible results throughout the study, whereas the performance of the trisox dendrimer system decreased monotonically. The reason for the different behaviour is the markedly lower activity of trisox-based catalysts relative to those based on the BOX ligand. This necessitated an increased reaction time for each cycle of the trisox derivatives, resulting in higher levels of catalyst leaching, which was attributed to a modification of the structure of the membrane by its exposure to the solvent trifluoroethanol at 40°C.

- Synthesis and Structure of α/δ-Hybrid Peptides - Access to Novel Helix Patterns in Foldamers
  Sharma, G. V. M.; Babu, B. S.; Ramakrishna, K. V. S.; Nagendar, P.; Kunwar, A. C.; Schramm, P.; Baldauf, C.; Hofmann, H.-J. *Chem. Eur. J.* **2009***, 15*, 5552-5566.
  Abstract:



Origami peptides: A novel class of foldamers consisting of α/δ-hybrid peptides has been investigated theoretically and experimentally by exploiting the rigidity of the side chain of a new δ-amino acid prepared from **D**-glucose and **D**-xylose with a furanose side chain (see figure).
Stimulated by an overview on all periodic folding patterns of α/δ-hybrid peptides with 1:1 alternating backbone provided by ab initio molecular orbital theory, the first representatives of this foldamer class were synthesized connecting novel C-linked carbo-δ-amino acid constituents and **L**-Ala. In agreement with theoretical predictions, extensive NMR spectroscopic analyses confirm the formation of new motifs of 13/11-mixed helical patterns in these peptides supported by the rigidity of the **D**-xylose side chain in the selected δ-amino acid constituents. Relationships between possible helix types in α/δ-hybrid peptides and their counterparts in other 1:1 hybrid peptide classes and native α-peptides are discussed; these indicate the high potential of these foldamers to mimic native peptide secondary structures. The design of α/δ-hybrid peptides provides an opportunity to expand the domain of foldamers and allows the introduction of desired functionalities through the α-amino acid constituents.

- Electrochemical Glucose Sensors and Their Applications in Diabetes Management
  Heller, A.; Feldman, B. *Chem. Rev.* **2008**, *108,* 2482-2505.
  Abstract:



About 6,000 peer reviewed articles have been published on electrochemical glucose assays and sensors, of which 700 were published in the 2005–2006 two-year period. Their number makes a full review of the literature, or even of the most recent advances, impossible. Nevertheless, this review should acquaint the reader with the fundamentals of the electrochemistry of glucose and provide a perspective of the evolution of the electrochemical glucose assays and monitors helping diabetic people, who constitute about 5% of the world's population. Because of the large number of diabetic people, no assay is performed more frequently than that of glucose. Most of these assays are electrochemical. The reader interested also in nonelectrochemical assays used in, or proposed for, the management of diabetes is referred to a 2007 review of Kondepati and Heise.
Historically, glucose electrooxidizing anodes have been studied not only because of their importance in diabetes management, but also in the context of glucose-O_2 biofuel cells. The objectives of biofuel cell research were generally overambitious. After 40 years of research, there is not a single biofuel

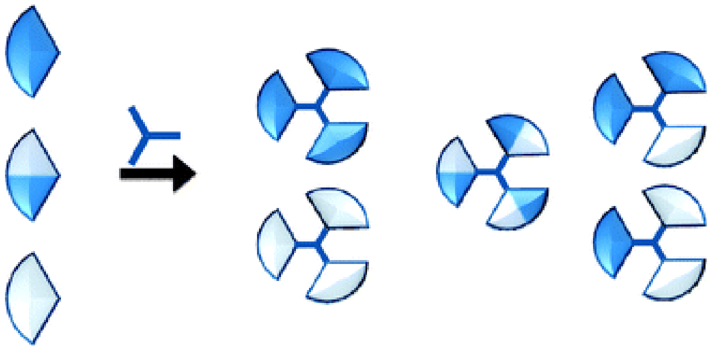
cell in use. Originally, the biofuel cells were intended to power cardiac assist devices (“artificial hearts”), then cardiac pacemakers, then to supply electrical power to homes or electrical grids by electrooxidizing glucose in, or derived of, wastes. The earliest studies already identified insurmountable power density and stability associated limitations, but these were not recognized by all investigators. Today, the power density of the glucose-O_2 biofuel cells remains about 10^4 fold below that required for a cardiac assist device and about 10^3 fold below that necessary to competitively supply power to the electrical grid. Furthermore, the operational lives of low-power-density biofuel cells for cardiac pacemakers are about 10^3 times shorter than required. Recent research, undertaken in the context of bioelectronic devices, has no defined application—the bioelectronic devices in which they are to be used have not been specified. Hence, this review covers only the glucose anodes of those disposable biofuel cells that might provide for a few weeks the low power required by subcutaneously implanted glucose sensors.

- Monitoring Rapid Chemical Communication in the Brain
  Robinson, D. L.; Hermans, A.; Seipel, A. T.; Wightman, R. M. *Chem. Rev.* **2008***, 108,* 2554-2584.
  <u>Abstract:</u>

Neurotransmitters are chemicals that are secreted by neurons and relay messages to target cells. The goal of in vivo electrochemistry is to provide a real-time view of neurotransmitters in the extracellular space of the brain. This may be done in brain slices or the intact brain of anesthetized animals to probe the basic functions that regulate neurotransmitter levels. In other experiments, the measurements need to be made in the brain of behaving animals so that correlations of neurotransmitter fluctuations and specific behaviors can be made. For the neurotransmitter dopamine this can be accomplished today by chemical sensing of this neurotransmitter with fast scan cyclic voltammetry (FSCV) at carbon-fiber microelectrodes. Dopamine is an important target because it is a central player in the brain “reward” system, although its precise function is not understood. Proposed roles for dopamine in reward have included the mediation of hedonia (pleasure), a messenger of incentive salience (wanting), or an error signal that promotes the learning associated with goal-directed behavior. These multiple interpretations of dopaminergic function have arisen because, until recently, a real-time view of dopamine and its actions in an awake, behaving animal was unavailable. At the same time, new electrochemical technologies are being developed to measure other neurotransmitter actions. Electrochemical approaches are well suited for this application because they allow a neurotransmitter to be measured with high time resolution, enabling its precise role in the execution of behavioral tasks to be investigated. In this review we will describe current methods to detect neurotransmitters and monitor their concentration dynamics within neural tissue.

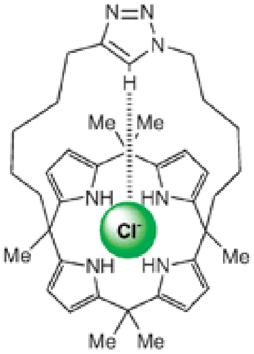
- Synthesis and characterisation of polyamide dendrimers with systematically varying surface

functionality.
Willcock, H.; Cooper, A. I.; Adams, D. J.; Rannard, S. P. *Chem. Commun.* **2009**, 3095 – 3097.
<u>Abstract:</u>



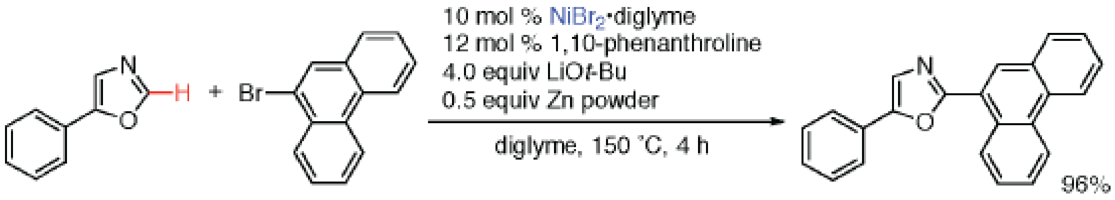
Remarkable changes of properties result from systematically varying the surface functionality of polyamide dendrimers within a single generation.

- 1,2,3-Triazole-strapped calix[4]pyrrole: a new membrane transporter for chloride.
  Fisher, M. G.; Gale, P. A.; Hiscock, J. H.; Hursthouse, M. B.; Light, M. E.; Schmidtchen, F. P.; Tong, C. C. *Chem. Commun.* **2009**, 3017 – 3019.
  <u>Abstract:</u>



A new triazole-strapped calix[4]pyrrole synthesised viaclick chemistry shows high affinity for chloride and lipid bilayer chloride transport properties.

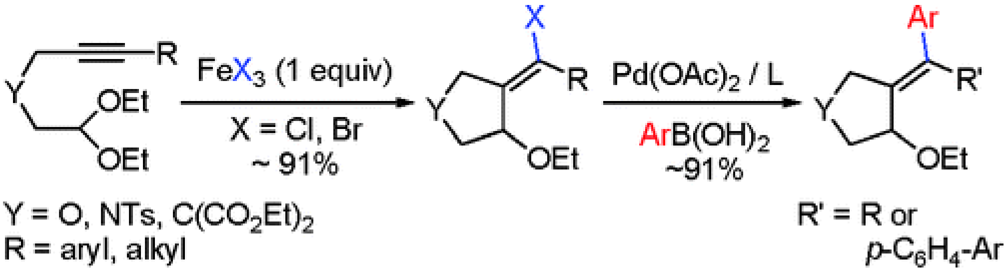
- Nickel-Catalyzed Direct Arylation of Azoles with Aryl Bromides
  Hachiya, H.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 1737-1740.
  <u>Abstract:</u>



Nickel catalyst systems for the direct C2 arylation of oxazoles and thiazoles have been developed. The catalyst systems are cost-efficient and allow the use of various aryl bromides in the C-H arylation of azoles.

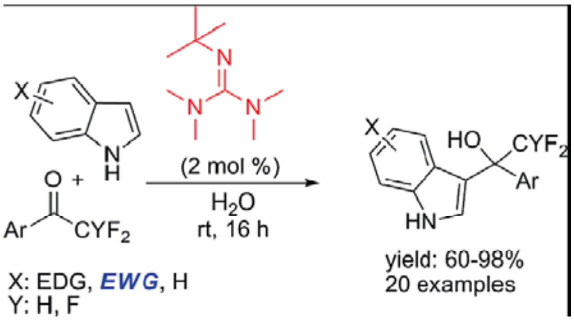
- Iron-Promoted Cyclization/Halogenation of Alkynyl Diethyl Acetals
  Xu, T.; Yu, Z.; Wang L. *Org. Lett.* **2009**, *11*, 2113-2116.

Abstract:



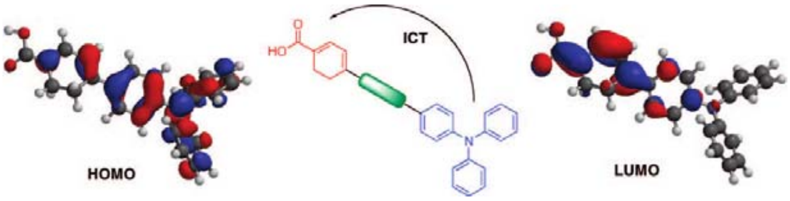
$FeCl_3$- and $FeBr_3$-promoted cyclization/halogenation of alkynyl diethyl acetals has been efficiently realized, selectively affording (*E*)-2-(1-halobenzylidene or alkylidene)-substituted five-membered carbo- and heterocycles which were then efficiently transformed to vinylarenes by Suzuki coupling. The present protocol has provided a new alternative route to vinylic C-Cl and C-Br bond formation.

- Efficient Guanidine-Catalyzed Alkylation of Indoles with Fluoromethyl Ketones in the presence of Water
  Bandini, M.; Sinisi, R. *Org. Lett.* **2009**, *11*, 2093-2096.
  Abstract:



A simple and efficient guanidine-catalyzed methodology for the direct preparation of trifluoromethyl-indolyl-phenylethanols in the presence of water is reported. This synthetically viable class of compounds is obtained in excellent yields (up to 98%) through Friedel-Crafts-type alkylation of indoles with aromatic fluoromethyl ketones. Exceptional reaction scope of indoles and alkylating agents is described.

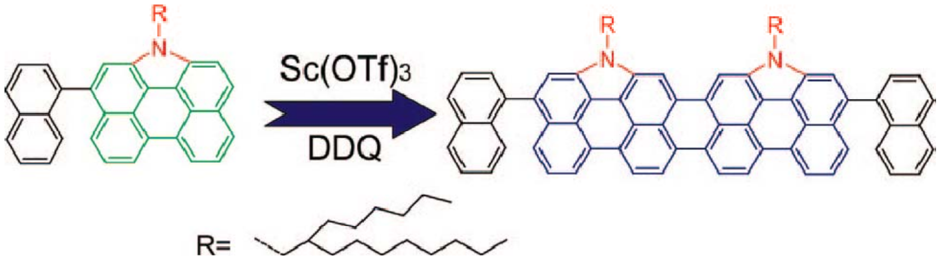
- Structurally Simple Dipolar Organic Dyes Featuring 1,3-Cyclohexadiene Conjugated Unit for Dye-Sensitized Solar Cells
  Chen, K.-F.; Hsu, Y.-C.; Wu, Q.; Yeh, M.-C. P.; Sun, S. S. *Org. Lett.* **2009**, *11*, 377-380.
  Abstract:



A series of structurally simple dipolar light-harvesting organic dyes featuring 1,3-cyclohexadiene in the aromatic π framework for dye-sensitized solar cells has been synthesized and characterized. The highest conversion efficiency of the DSSCs based on these dyes can reach up to 4.4%.

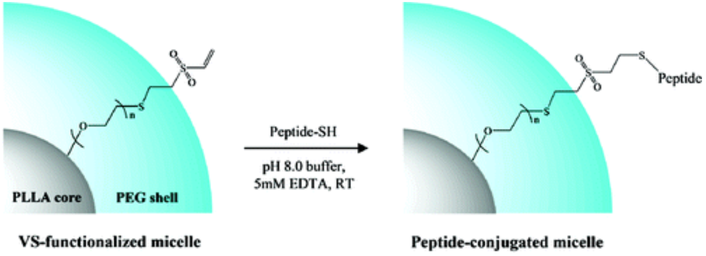
- Bis-N-Annulated Quaterrylene: An Approach to Processable Graphene Nanoribbons
  Li, Y.; Wang, Z. *Org. Lett.* **2009**, *11*, 1385-1387.

Abstract:



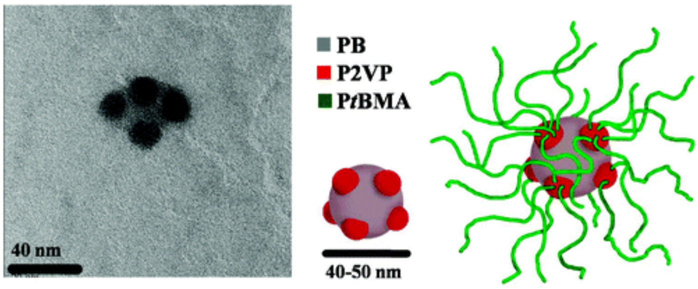
A new efficient synthetic method toward processable bis-N-annulated quaterrylene from easily available N-annulated perylene derivatives, which is conducted by DDQ/Sc(OTf)3 oxidative coupling and ring fusion, is reported. In light of the good processability and the strong electrondonating ability, which is evidenced from the low oxidative potentials, bis-N-annulated quaterrylene is very promising for use as functional components in molecular devices.

- Vinyl Sulfone-Terminated PEG-PLLA Diblock Copolymer for Thiol-Reactive Polymeric Micelle.
  Bae, J. W.; Lee, E.; Park, K. M.; Park, K. D. *Macromolecules* **2009**, *42*, 3437-3442.
  Abstract:



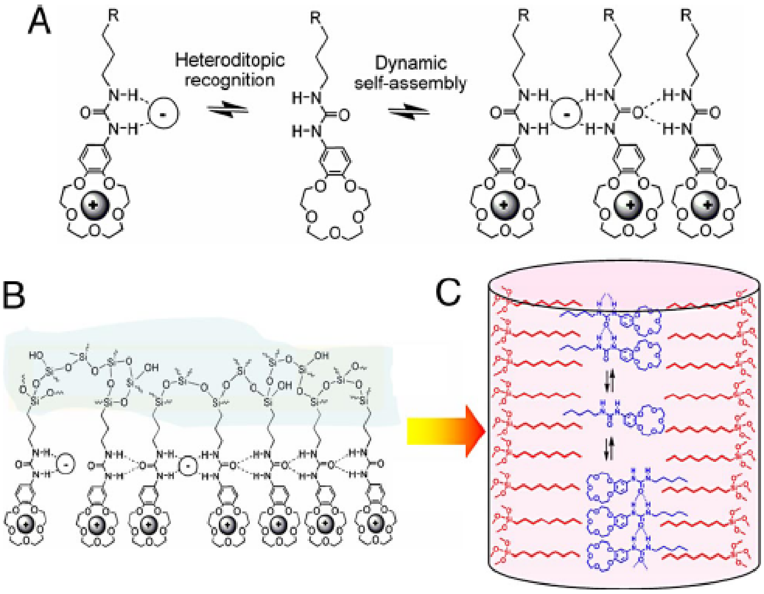
Vinyl sulfone-terminated polyethylene glycol-poly(L-lactide) (VS-PEG-PLLA) diblock copolymer was designed as an amphiphilic structure containing a VS group with high reactivity toward thiols. Prior to the copolymer synthesis, heterobifunctional PEG with a VS group at one terminus was prepared and then PLLA was introduced to the other end of PEG. The chemical structure and molecular weight of the resulting products was assigned by 1H NMR and GPC. As micellar properties of VS-PEG-PLLA under aqueous environment, the critical micelle concentration and mean size of VS-PEG-PLLA were found to be approximately 59.8 mg/L and 34 nm, respectively. Kinetic studies of the VS-functionalized PEG-PLLA micelle showed that the reaction rates were affected by various factors but most of cysteine-contained peptides reacted rapidly within 1 h V*ia* Michaeltype addition. Therefore, this thiol-reactive polymeric micelle is expected to be very useful for a functional nanocarrier system through the effective conjugation of cysteine-containing peptides or proteins.

- Multicompartment Core Micelles of Triblock Terpolymers in Organic Media.
  Schacher, F.; Walther, A.; Ruppel, M.; Drechsler, M.; Müller, A. H. E. *Macromolecules* **2009**, *42*, 3540-3548.
  Abstract:



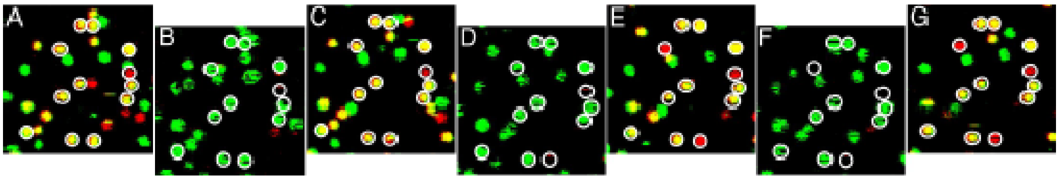
The formation of multicompartment micelles featuring a “spheres on sphere” core morphology in acetone as a selective solvent is presented. The polymers investigated are ABC triblock terpolymers, polybutadiene*b*-poly(2-vinyl pyridine)-*b*-poly(*tert*-butyl methacrylate) (BVT), which were synthesized via living sequential anionic polymerization in THF. Two polymers with different block lengths of the methacrylate moiety were studied with respect to the formation of multicompartmental aggregates. The micelles were analyzed by static and dynamic light scattering as well as by transmission electron microscopy. Cross-linking of the polybutadiene compartment could be accomplished via two different methods, “cold vulcanization” and with photopolymerization after the addition of a multifunctional acrylate. In both cases, the multicompartmental character of the micellar core is fully preserved, and the micelles could be transformed into core-stabilized nanoparticles. The successful cross-linking of the polybutadiene core is indicated by 1H NMR and by the transfer of the aggregates into nonselective solvents such as THF or dioxane.

- Dynamic hybrid materials for constitutional self-instructed membranes
  Cazacu, A.; Legrand, Y.-M.; Pasc, A.; Nasr, G.; Van der Lee, A.; Mahon, E.; Barboiu, M. *Proc. Nat. Acad. Sci.* **2009**, *106*, 8117–8122.
  Abstract:



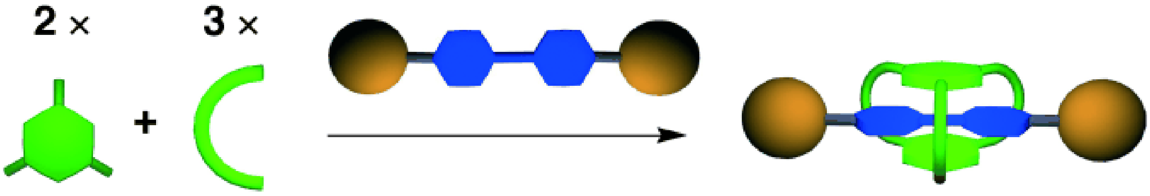
Constitutional self-instructed membranes were developed and used for mimicking the adaptive structural functionality of natural ionchannel systems. These membranes are based on dynamic hybrid materials in which the functional self-organized macrocycles are reversibly connected with the inorganic silica through hydrophobic noncovalent interactions. Supramolecular columnar ion-channel architectures can be generated by reversible confinement within scaffolding hydrophobic silica mesopores. They can be structurally determined by using X-ray diffraction and morphologically tuned by alkali-salts templating. From the conceptual point of view, these membranes express a synergistic adaptive behavior: the simultaneous binding of the fittest cation and its anion would be a case of ''homotropic allosteric interactions,'' because in time it increases the transport efficiency of the pore-contained superstructures by a selective evolving process toward the fittest ion channel. The hybrid membranes presented here represent dynamic constitutional systems evolving over time to form the fittest ion channels from a library of molecular and supramolecular components, or selecting the fittest ion pairs from a mixture of salts demonstrating flexible adaptation.

- Controlling the fluorescence of ordinary oxazine dyes for single-molecule switching and superresolution microscopy
  Vogelsang, J.; Cordes, T.; Forthmann, C.; Steinhauer, C.; Tinnefeld, P *Proc. Nat. Acad. Sci.* **2009**, *106*, 8107–8112.
  Abstract:



Fluorescent molecular switches have widespread potential for use as sensors, material applications in electro-optical data storages and displays, and superresolution fluorescence microscopy. We demonstrate that adjustment of fluorophore properties and environmental conditions allows the use of ordinary fluorescent dyes as efficient single-molecule switches that report sensitively on their local redox condition. Adding or removing reductant or oxidant, switches the fluorescence of oxazine dyes between stable fluorescent and nonfluorescent states. At low oxygen concentrations, the off-state that we ascribe to a radical anion is thermally stable with a lifetime in the minutes range. The molecular switches show a remarkable reliability with intriguing fatigue resistance at the single-molecule level: Depending on the switching rate, between 400 and 3,000 switching cycles are observed before irreversible photodestruction occurs. A detailed picture of the underlying photoinduced and redox reactions is elaborated. In the presence of both reductant and oxidant, continuous switching is manifested by ''blinking'' with independently controllable on- and off-state lifetimes in both deoxygenated and oxygenated environments. This ''continuous switching mode'' is advantageously used for imaging actin filament and actin filament bundles in fixed cells with subdiffraction-limited resolution.

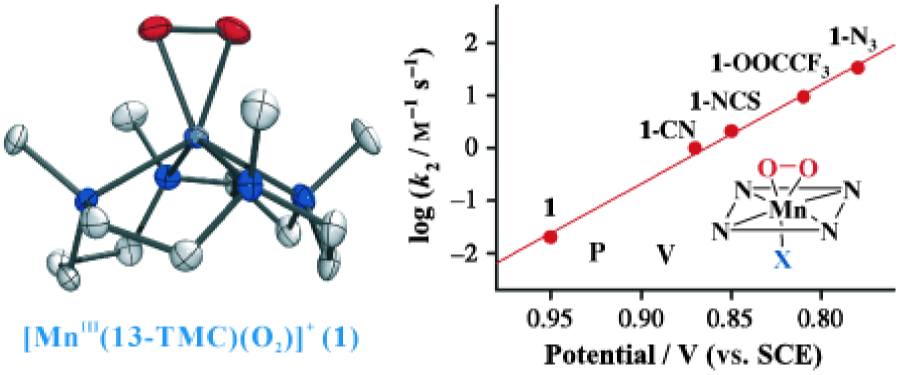
- Linear p-Acceptor-Templated Dynamic Clipping to acrobicycles and [2]Rotaxanes
  Klivansky, L. M.; Koshkakaryan, G.; Cao, D.; Liu, Y. *Angew. Chem. Int. Ed*. **2009**, *48*, 4185 – 4189.
  Abstract:



Cage me! A linear dumbbell-shaped bipyridinium molecule can template cage formation around itself through sixfold imine bond formation to give an interlocked [2]rotaxane as the single product (see

picture). This highly efficient [2+3] clipping occurs despite the symmetry mismatch between the template and the formed macrobicycle.

- Structural Characterization and Remarkable Axial Ligand Effect on the Nucleophilic Reactivity of a Nonheme Manganese(III)–Peroxo Complex
  Annaraj, J.; Cho, J.; Lee, Y.-M.; Kim, S. Y.; Latifi, R.; de Visser, S. P.; Nam, W. *Angew. Chem. Int. Ed*. **2009**, *48*, 4150 –4153.
  Abstract:



The dark side of the Mn: A manganese(III) complex bearing a 13-membered macrocyclic ligand (**1**, see picture) binds a peroxo ligand in a side-on η^2 fashion. The reactivity of **1** is influenced by the introduction of anionic ligands *trans* to the peroxo group. Electronic and structural changes upon *trans*-ligand binding explain the increased nucleophilicity of the resulting complexes **1**-X.