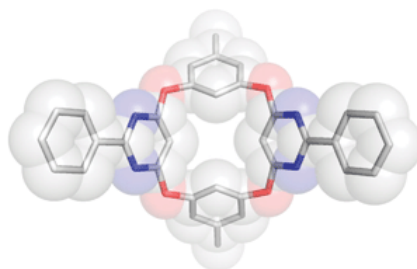


- Oxacalix[n](het)arenes
Maes, W.; Dehaen, W. *Chem. Soc. Rev.* **2008**, *37*, 2393 – 2402.

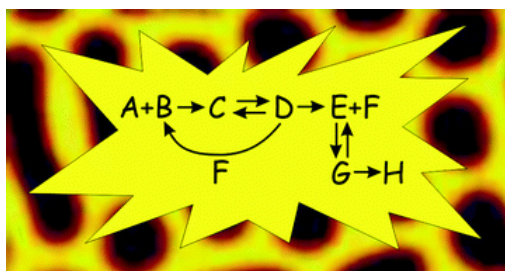
Abstract:



Oxacalix[n]arenes, reassessed members of the calixarene family in which the traditional methylene bridges are replaced by oxygen atoms, have emerged as a promising class of macrocycles in recent years. This *tutorial review* summarizes the synthetic progress made in the field during the last few years and aims to stimulate its current evolution from a merely synthetic to a more applied branch of macro- and supramolecular chemistry.

- Systems chemistry
Ludlow, R. F.; Otto, S. *Chem. Soc. Rev.* **2008**, *37*, 101 – 108.

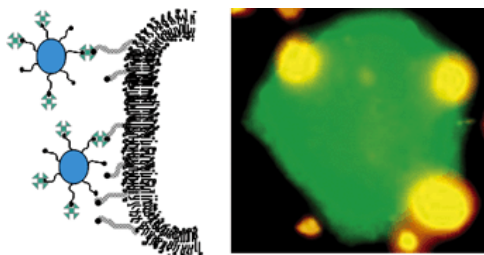
Abstract :



The study of complex mixtures of interacting synthetic molecules has historically not received much attention from chemists, even though research into complexity is well established in the neighbouring fields. However, with the huge recent interest in systems biology and the availability of modern analytical techniques this situation is likely to change. In this *tutorial review* we discuss some of the incentives for developing systems chemistry and we highlight the pioneering work in which molecular networks are making a splash. A distinction is made between networks under thermodynamic and kinetic control. The former include dynamic combinatorial libraries while the latter involve pseudo-dynamic combinatorial libraries, oscillating reactions and networks of autocatalytic and replicating compounds. These studies provide fundamental insights into the organisational principles of molecular networks and how these give rise to emergent properties such as amplification and feedback loops, and may eventually shed light on the origin of life. The knowledge obtained from the study of molecular networks should ultimately enable us to engineer new systems with properties and functions unlike any conventional materials.

- Self-Assembly of Cell-Microparticle Hybrids
Krishnamachari, Y.; Pearce, M. E.; Salem, A. K. *Adv. Mater.* **2008**, *20*, 989-993.

Abstract:

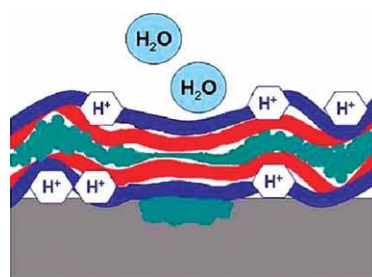


Synthetic-biological hybrids of biodegradable microparticles and transfected cells are assembled, as schematically illustrated in the figure. The cells are surface-functionalized with biotin and the particle surface is also engineered with biotin. Avidin is then used as a bridging protein to bind together the microparticles and the surface-functionalized cells.

- Self-Healing Anticorrosion Coatings Based on pH-Sensitive Polyelectrolyte/Inhibitor Sandwichlike Nanostructures

Andreeva, D. V.; Fix, D.; Möhwald, H.; Shchukin, D. G. *Adv. Mater.* **2008**, *20*, 2789-2794.

Abstract:

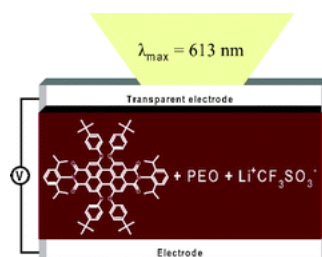


An anticorrosion layer of a smart polymer coating is developed. The nature and properties of the coating simultaneously provide three mechanisms of corrosion protection: passivation of the metal degradation by controlled release of an inhibitor, buffering of pH changes at the corrosive area by polyelectrolyte layers, and self-curing of the film defects due to the mobility of the polyelectrolyte constituents in the layer-by-layer assembly.

- Synthesis and utilization of perylene-based *n*-type small molecules in light-emitting electrochemical cells

Hill, Z. B. ; Rodovsky, D. B. ; Leger, J. M. ; Bartholomew, G. P. *Chem. Commun.* **2008**, 6594 – 6596.

Abstract :



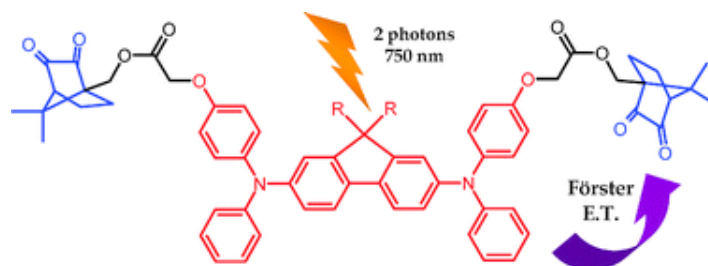
We report the synthesis of a soluble perylene-based small molecule for use as an *n*-type emissive material for organic optoelectronic device applications, and demonstrate the material in a light-emitting electrochemical cell configuration.

- Two-photon absorption and polymerization ability of intramolecular energy transfer based photoinitiating systems

Jin, M. ; Malval, J.-P. ; Versace, D.-P. ; Morlet-Savary, F. ; Chaumeil, H. ; Defoin, A. ; Allonas, X. ; Fouassier, J.-P. *Chem. Commun.* **2008**, 6540 – 6542.

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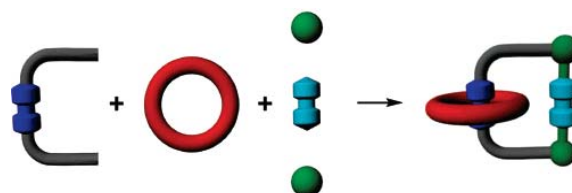
Abstract :



We design a new photoinitiating system where the two-photon absorption of a 2,7 bisaminofluorene moiety leads to the photoactivation of a camphorquinone subunit through a Förster-type intramolecular energy transfer: the application to a two-photon polymerization reaction is demonstrated.

- Palladium(II)-Directed Self-Assembly of Dynamic Donor-Acceptor [2]Catenanes
Liu Y.; Bruneau A.; He J.; Abliz Z. *Org. Lett.* **2008**, *10*, 765-768.

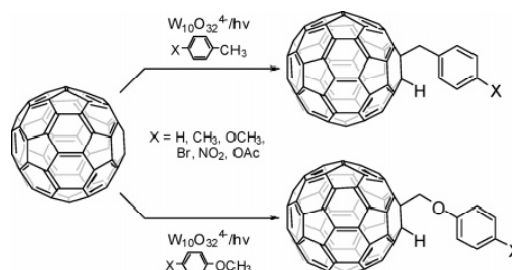
Abstract :



Highly efficient syntheses of donor-acceptor [2]catenanes were developed using a combination of templation and reversible metal-ligand coordination. The desired [2]catenanes were obtained within minutes through a five-component assembly, involving a donor-containing crown ether, an acceptor-containing ligand, two Pd(II) metal centers, and a dipyrindyl ligand. The [2]catenane formation was characterized by ^1H NMR and UV-vis spectroscopies and cold-spray ionization mass spectrometry. In particular, great translational selectivity was observed when a crown ether with two different donor units was employed.

- Decatungstate-Mediated Radical Reactions of C₆₀ with Substituted Toluenes and Anisoles: A New Photochemical Functionalization Strategy for Fullerenes
Tzirakis M. D.; Orfanopoulos M. *Org. Lett.* **2008**, *10*, 873-876.

Abstract :



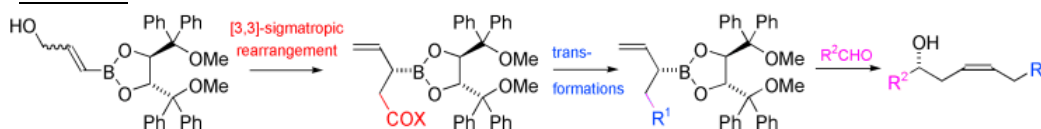
A convenient, highly efficient, decatungstate-mediated chemical methodology to functionalize fullerenes is demonstrated. A variety of radicals have been generated by the photochemical interaction of tetrabutylammonium decatungstate $[(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}]$ and para-substituted toluenes,

anisoles, and thioanisole and effectively trapped by the [60]fullerene affording the corresponding 1,2-dihydro[60]fullerene monoadducts in moderate to good yields.

4

- Diastereo- and Enantiomerically Pure Allylboronates: Their Synthesis and Scope
Pietruszka, J.; Schöne, N.; Frey, W.; Grundl, L. *Chem. Eur. J.* **2008**, *14*, 5178-5197.

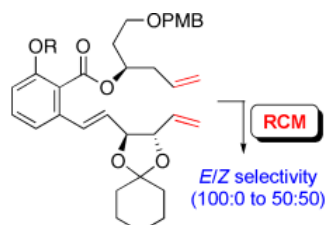
Abstract:



Allylboronates are highly attractive reagents for allyl additions. Enantiomerically pure, stable reagents with a stereogenic centre in α -position to boron are especially versatile, albeit often difficult to synthesize. Starting from boron-containing allyl alcohols **6** and **7**, which are discussed in detail herein, a set of reagents were obtained via [3,3]-sigmatropic rearrangements and consecutive transformations in the side chain. The configurations could be established first by chemical correlation, but also by X-ray crystallography (**16**, **18**, **34**, and **39**). Allyl additions were performed resulting in the formation of predominantly (*Z*)-configured homoallylic alcohols (**31**, **43-45**) with high enantiomeric excess. Detailed investigations on the matched-mismatched interaction between the reagents **15/16** (and *ent*-**15/ent**-**16**, respectively) and isopropylidene glyceraldehyde **42 d** are presented.

- Kinetically Controlled Ring-Closing Metathesis: Synthesis of a Potential Scaffold for 12-Membered Salicylic Macrolides
Matsuya, Y.; Takayanagi, S.; Nemoto, H. *Chem. Eur. J.* **2008**, *14*, 5275-5281.

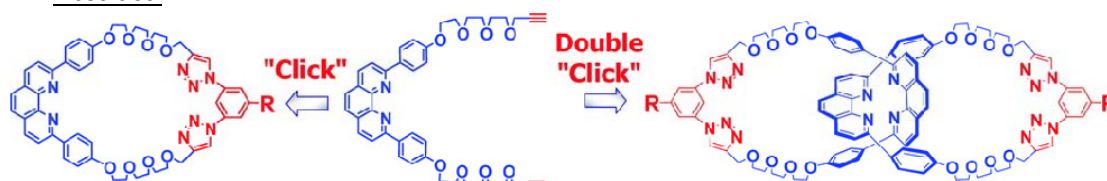
Abstract:



For the synthesis of a 12-membered salicylic macrolide scaffold, ring-closing metathesis (RCM) of a ω -diene compound was planned. The stereochemical outcome of the RCM reaction changed depending on the type of Ru catalyst that was used; a “first-generation” Grubbs catalyst produced exclusively the *E* isomer and “second-generation” catalysts provided a mixture of the *E* and *Z* isomers under kinetic control (not thermodynamic control). Considerations for the *E/Z* selectivity are described.

- General Method for Synthesis of Functionalized Macrocycles and Catenanes Utilizing “Click” Chemistry
Megiatto, J. D.; Schuster, D. J. *Am. Chem. Soc.* **2008**, *130*, 12872–12873.

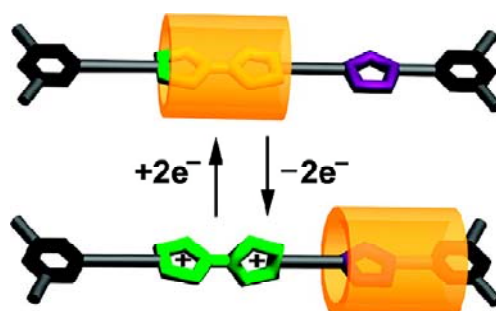
Abstract:



A new protocol for efficient and high yield synthesis of functionalized macrocycles and catenanes has been developed using "click" chemistry in combination with Sauvage's metal template route to interlocked structures. The procedure involves introduction of terminal alkyne moieties on a symmetrical 2,9-diaryl-1,10-phenanthroline (phen) building block, followed by double-"click" ring closure using aryl 3,5-diazides in the presence of CuI, sodium ascorbate, the base DBU and a sulfonated phenanthroline ligand in an oxygen-free 7:3:1 ethanol/water/toluene mixture at 70 °C. Utilizing acetal and vinyl substituted diazides, the corresponding bistriazole/phen macrocycles, characterized spectroscopically, were obtained in 65–70% yield. Formation of a binary Cu(I) complex of the diethynylphen ligand followed by reaction with aryl 3,5-diazides using a modified procedure affords the corresponding difunctionalized catenane in one step in 85–92% yield. The initial catenanes obtained after workup are Cu-free. Reintroduction of Cu(I) using $\text{Cu}(\text{CH}_3\text{CN})_4^+\text{PF}_6^-$ gives the metallocatenanes, whose spectral properties are identical to those of related $(\text{phen})_2\text{Cu}(\text{I})$ catenanes reported by Sauvage and co-workers. This methodology provides ready access to functionalized interlocked structures, which can be used as intermediates in the preparation of a variety of new materials, including compounds of interest as artificial photosynthetic systems.

- A Redox-Switchable α -Cyclodextrin-Based [2]Rotaxane
Zhao, Y.; Dichtel, W. R.; Trabolsi, A.; Saha, S.; Aprahamian, I.; Stoddart, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 11294–11296.

Abstract:

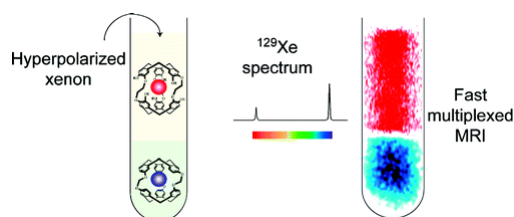


A bistable [2]rotaxane comprising an α -cyclodextrin (α -CD) ring and a dumbbell component containing a redox-active tetrathiafulvalene (TTF) ring system within its rod section has been synthesized using the Cu(I)-catalyzed azide–alkyne cycloaddition, and the redox-driven movements of the α -CD ring between the TTF and newly formed triazole ring systems have been elucidated. Microcalorimetric titrations on model complexes suggested that the α -CD ring prefers to reside on the TTF rather than on the triazole ring system by at least an order of magnitude. The fact that this situation does pertain in the bistable [2]rotaxane has not only been established quantitatively by electrochemical experiments and backed up by spectroscopic and chiroptical measurements but also been confirmed semiquantitatively by the recording of numerous cyclic voltammograms which point, along with the use of redox-active chemical reagents, to a mechanism of switching that involves the oxidation of the neutral TTF ring system to either its radical cationic ($\text{TTF}^{\bullet+}$) or dicationic (TTF^{2+}) counterparts, whereupon the α -CD ring, moves along the dumbbell to encircle the triazole ring system. Since redox control by both chemical and electrochemical means is reversible, the switching by the bistable [2]rotaxane can be reversed on reduction of the $\text{TTF}^{\bullet+}$ or TTF^{2+} back to being a neutral TTF.

- Sensitivity and Multiplexing Capabilities of MRI Based on Polarized ^{129}Xe Biosensors
Berthault, P.; Bogaert-Buchmann, A.; Desvaux, H.; Huber, G.; Boulard, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16456–16457.

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Abstract:

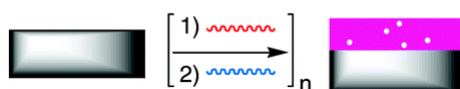


^{129}Xe MRI is applied to cage molecules in which hyperpolarized xenon exhibits a specific spectral signature. In a few tens of seconds a net spatial discrimination is achieved between xenon in two different hosts dissolved in two immiscible media at submillimolar concentrations by using a gradient echo sequence with interleaved frequency selection. This high sensitivity is afforded not only by the hyperpolarized state of xenon but also by the continuous xenon in-out exchange that enables replenishment of the detected signal. Moreover in this direct approach, simultaneous detection of xenon in two different cage molecules is possible. This experiment on a model system is an important step toward *in vivo* multiplexed MRI using laser-polarized xenon.

- Defects in a Polyelectrolyte Multilayer: The Inside Story
Wang, Y.; Stedronsky, E.; Regen, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 16510–16511.

Abstract:

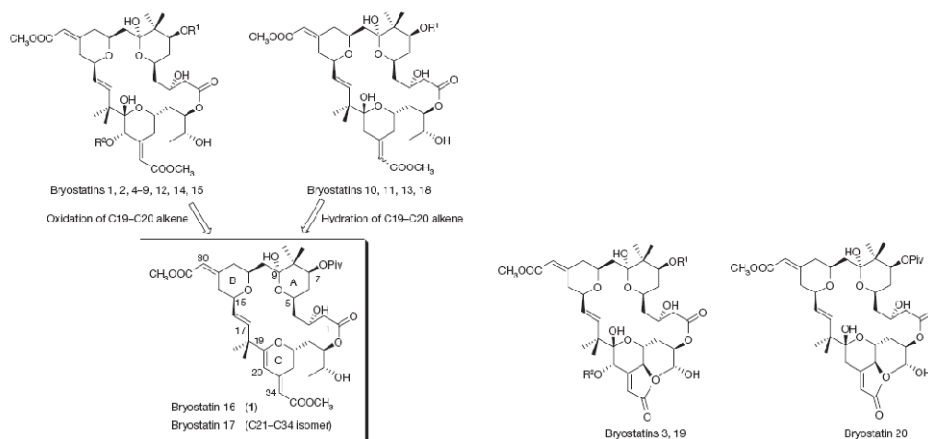
Layer-by-Layer Deposition of Polyelectrolytes



Moderate changes in the concentration of poly(sodium 4-styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) used in fabricating polyelectrolyte multilayers (PEMs) have been found to strongly affect the formation of *defects* (i.e., gaps) within these films, as revealed by gas permeation selectivity measurements. Thus, PEMs made from 14 alternating layers of PSS and PAH under “high” concentration conditions (15.0 mM in repeat units) exhibit He/N₂ permeation selectivities that are greater than 200. In sharp contrast, analogous films of similar thickness that are made from 24 alternating layers of PSS and PAH under “low” concentration conditions (1.0 mM in repeat units) showed no significant He/N₂ permeation selectivity, reflecting the presence of defects. Analogous PEMs that were fabricated from 14 alternating layers of PSS and PAH, using 1.0 mM PSS and PAH in the presence of added NaCl, where reduced viscosities and polymer conformations were matched with those found under high concentration conditions, exhibited the same thicknesses and very similar barrier properties.

- Total synthesis of bryostatin 16 using atom-economical and chemoselective approaches.
Trost, B. M. & Dong, G. *Nature* **2008**, *456*, 485-488.

Abstract:

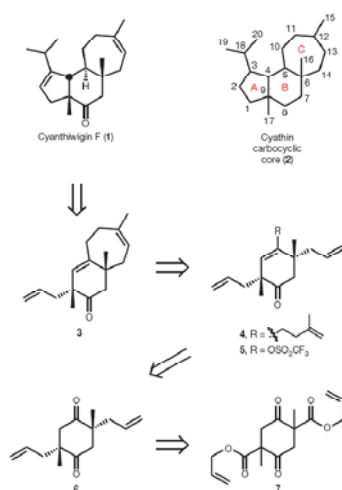


Of the concepts used to improve the efficiency of organic syntheses, two have been especially effective: atom economy (the use of routes in which most of the atoms present in the reactants also end up in the product) and chemoselectivity (the use of reactions that take place only at desired positions in a molecule). Synthesis of complex natural products is the most demanding arena in which to explore such principles. The bryostatin family of compounds are especially interesting targets, because they combine structural complexity with promising biological activity. Furthermore, synthetic routes to some bryostatins have already been reported, providing a benchmark against which new syntheses can be measured. Here we report a concise total synthesis of bryostatin 16 (1), a parent structure from which almost all other bryostatins could in principle be accessed. Application of atom-economical and chemoselective reactions currently under development provides ready access to polyhydropyran motifs in the molecule, which are common structural features of many other natural products. The most notable transformations are two transition-metal-catalysed reactions. The first is a palladium-catalysed reaction of two different alkynes to form a large ring. The product of this step is then converted into a dihydropyran (the 'C ring' of bryostatins) in the second key reaction, which is catalysed by a gold compound. Analogues of bryostatin that do not exist in nature could be readily made by following this route, which might allow the biological activity of bryostatins to be fine-tuned

- The total synthesis of (-)-cyanthiwigin F by means of double catalytic enantioselective alkylation

Enquist Jr, J. A.; Stoltz, B. M. *Nature* **2008**, *453*, 1228-1231.

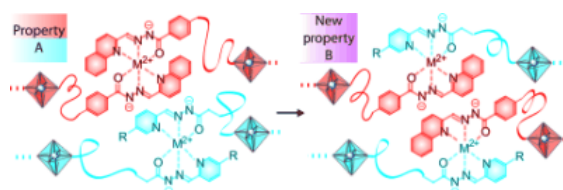
Abstract:



Double catalytic enantioselective transformations are powerful synthetic methods that can facilitate the construction of stereochemically complex molecules in a single operation. In addition to generating two or more stereocentres in a single reaction, multiple asymmetric reactions also impart increased enantiomeric excess to the final product in comparison with the analogous single transformation. Furthermore, multiple asymmetric operations have the potential to independently construct several stereocentres at remote points within the same molecular scaffold, rather than relying on pre-existing chiral centres that are proximal to the reactive site. Despite the inherent benefits of multiple catalytic enantioselective reactions, their application to natural product total synthesis remains largely underutilized. Here we report the use of a double stereoablative enantioselective alkylation reaction in a concise synthesis of the marine diterpenoid (-)-cyanthiwigin F. By employing a technique for independent, selective formation of two stereocentres in a single stereoconvergent operation, we demonstrate that a complicated mixture of racemic and meso diastereomers may be smoothly converted to a synthetically useful intermediate with exceptional enantiomeric excess. The stereochemical information generated by means of this catalytic transformation facilitates the easy and rapid completion of the total synthesis of this marine natural product.

- Metallodynamers: Neutral Double-Dynamic Metallosupramolecular Polymers
Chow, C.-F.; Fujii, S.; Lehn, J.-M. *Chem. Asian J.* **2008**, *3*, 1324-1335.

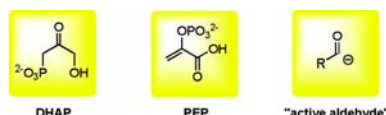
Abstract:



A good mix up: Self-assembly polymerization produces dynamic metallosupramolecular polymers (metallodynamers) based on metal-ligand coordination. These polymers can modify their constitution with another metallodynamer through ligand exchange at the metal coordination site. As a result, their mechanical and optical properties are changed dramatically.

- Lessons from Nature: Biomimetic Organocatalytic Carbon–Carbon Bond Formations
Enders, D.; Narine, A. A. *J. Org. Chem.* **2008**, *73*, 7857–7870.

Abstract:



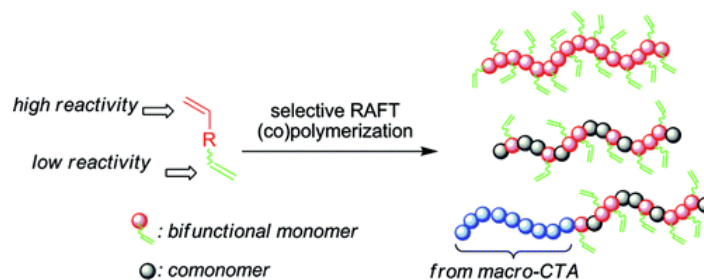
Nature utilizes simple C₂ and C₃ building blocks, such as dihydroxyacetone phosphate (DHAP), phosphoenolpyruvate (PEP), and the “active aldehyde” in various enzyme-catalyzed carbon–carbon bond formations to efficiently build up complex organic molecules. In this Perspective, we describe the transition from using enantiopure chemical synthetic equivalents of these building blocks, employing our SAMP/RAMP hydrazone methodology and metalated chiral α -amino nitriles, to the asymmetric organocatalytic versions developed in our laboratory. Following this biomimetic strategy, the DHAP equivalent 2,2-dimethyl-1,3-dioxan-5-one (dioxanone) has been used in the proline-catalyzed synthesis of carbohydrates, aminosugars, carbasugars, polyoxamic acid, and various sphingosines. Proline-catalyzed aldol reactions involving a PEP-like equivalent have also allowed for the asymmetric synthesis of ulosonic acid precursors. By mimicking the “active aldehyde”

nucleophilic acylations in Nature catalyzed by the thiamine-dependent enzyme, transketolase, enantioselective *N*-heterocyclic carbene-catalyzed benzoin and Stetter reactions have been developed. Finally, based on Nature's use of domino reactions to convert simple building blocks into complex and highly functionalized molecules, we report on our development of biomimetic asymmetric multicomponent domino reactions which couple enamine and iminium catalysis.

- Well-Defined Polymers Bearing Pendent Alkene Functionalities via Selective RAFT Polymerization.

Ma, J.; Cheng, C.; Sun, G.; Wooley, K. L. *Macromolecules* **2008**, *41*, 9080–9089.

Abstract :



A facile synthetic approach for the preparation of well-defined copolymers bearing pendent alkene functionalities was established by selective reversible addition–fragmentation chain transfer (RAFT) (co)polymerization. A divinyl monomer, 4-(3'-buten-1'-oxy)-2,3,5,6-tetrafluorostyrene (**1**), with a styrenyl group and a pendent alkene group was synthesized. Because of a very high reactivity of the styrenyl group relative to the alkene group in **1**, functional fluorocopolymers with both well-defined structures and pendent alkene groups were prepared by RAFT polymerization of **1** and copolymerization of **1** with pentafluorostyrene (PFS). Alkene-functionalized diblock copolymers were also prepared by RAFT copolymerizations of **1** with PFS or styrene, extending from a poly(styrene-*alt*-maleic anhydride) macrochain transfer agent. Hydrolysis and aminolysis of these copolymers resulted in amphiphilic diblock fluorocopolymers with alkene-functionalized hydrophobic segments, which were shown to form internally functionalized micelles in THF–water

- Synthesis and Micellization of Coil–Rod–Coil Ruthenium(II) Terpyridine Assemblies
Chiper, M.; Winter, A.; Hoogenboom, R.; Egbe, D. A. M.; Wouters, D.; Hoepfner, S.; Fustin, C.-A.; Gohy, J.-F.; Schubert, U. S. *Macromolecules* **2008**, *41*, 8823–8831.

Abstract :

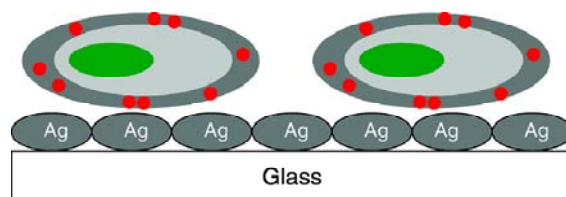


Four different coil–rod–coil metallo-supramolecular amphiphilic copolymers have been synthesized via Ru(II) terpyridine complexation, using monoterpyridine end-functionalized poly(ethylene glycol) as hydrophilic block **A** and different rigid-rod conjugated ditopic terpyridyl ligands as hydrophobic segment **B**. Those structures are reminiscent of **ABA** triblock copolymers. Herein, we report for the first time the synthesis and characterization as well as the photophysical and electrochemical properties of these novel Ru(II) **ABA** assemblies. The aqueous self-assembly of these synthesized materials was studied by cryo-transmission electron microscopy and dynamic light scattering, demonstrating a significant influence of the various middle segments **B** on the size of the obtained micelles.

- Enhanced Fluorescence Images for Labeled Cells on Silver Island Films

Zhang, J.; Fu, Y.; Liang, D.; Zhao, R. Y.; Lakowicz, J. R. *Langmuir* **2008**, *24*, 12452-12457.

Abstract:

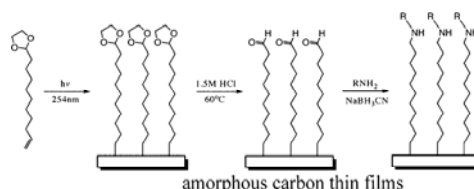


Silver island films (SIFs) were deposited on glass substrates to serve as supports. T-Lymphocytic (PM1) cell lines were labeled by Alexa Fluor 680-dextran conjugates on the membranes or by YOYO in the nuclei. The fluorescence images of the cell lines were recorded in the emission intensity and lifetime using scanning confocal microscopy. The fluorescence signals by the fluorophores bound on the cell membranes were enhanced significantly by SIF supports as compared with those on the glass. In addition to the increase in the intensity, there was a dramatic shortening of the emission lifetime. In contrast to the Alexa Fluor 680 fluorophores on the membranes, the YOYO fluorophores intercalated in the cell nuclei were not influenced significantly by the silver islands. This result can be interpreted by an effect of the distance on coupling between the fluorophores and metal particles: the fluorophores on the cell membranes are localized within, but the fluorophores in the cell nuclei are beyond the region of metal-enhanced fluorescence. Thus, the metal supports can be used to improve the detection sensitivity for target molecules on cell surfaces when they are fluorescently labeled.

- Aldehyde-Terminated Amorphous Carbon Substrates for the Fabrication of Biomolecule Arrays

Lockett, M. R.; Shortreed, M. R.; Smith, L. M. *Langmuir* **2008**, *24*, 9198-9203.

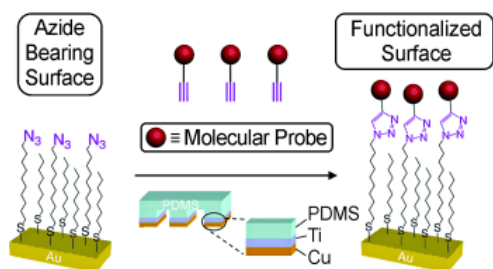
Abstract:



Amorphous carbon thin films are easily deposited at room temperature, readily functionalized with alkene-containing molecules through a UV photochemical reaction, and provide a robust surface capable of supporting chemical and biomolecule array fabrication. Aldehyde-terminated amorphous carbon substrates were fabricated via the attachment of a 2-(10-undecen-1-yl)-1,3-dioxolane molecule. The surfaces were then deprotected in 1.5 M HCl to yield an aldehyde-terminated surface that is readily reactive with amine containing molecules. An array of amine-modified oligonucleotides was prepared on aldehyde-terminated surfaces prepared on both amorphous carbon and on gold self-assembled monolayers, and the fluorescence background, feature signal-to-noise ratio, and hybridization densities were compared. The aldehyde-terminated amorphous carbon substrates offer inherently lower background fluorescence intensity and a greater number of hybridization-accessible sites.

- Heterogeneous Catalysis through Microcontact Printing

Spruell, J. M.; Sheriff, B. A.; Rozkiewicz, D. I.; Dichtel, W. R.; Rohde, R. D.; Reinhoudt, D. N.; Stoddart, J. F.; Heath, J. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 9927-9932.

Abstract:

Minting a Stamp: The preparation of copper metal-coated elastomeric stamps and their use in catalyzing the Cu-catalyzed azide-alkyne cycloaddition reaction heterogeneously through microcontact printing is described (see scheme). This StampCat process is compared to other conventional surface-functionalization techniques, including traditional microcontact printing and solution-surface-based reactions.