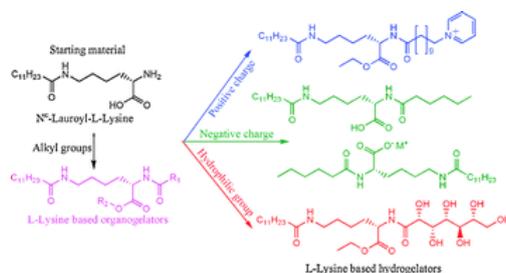


- L-Lysine-based low-molecular-weight gelators
Suzuki, M.; Hanabusa, K. *Chem. Soc. Rev.* **2009**, *38*, 967 – 975.

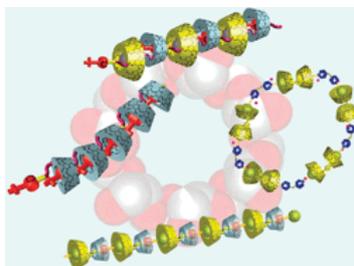
Abstract:



Low-molecular-weight gelators form supramolecular gels in organic fluids, aqueous solutions and both organic and aqueous solutions through supramolecular interactions such as hydrogen-bonding, van der Waals, hydrophobic, π -stacking, coordination, donor–acceptor and charge-transfer interactions. Molecules having chirality, especially, L-amino acids, are often used as a platform of low-molecular-weight gelators. This *tutorial review* highlights recent and current advances in low-molecular-weight gelators based on L-lysine. L-Lysine based gelators are prepared through easy synthetic procedures, and some classes of gelators are synthesized by the introduction of various functional groups. In this review, the synthesis of organogelators, hydrogelators and amphiphilic gelators and their gelation properties are discussed.

- Cyclodextrin-based supramolecular polymers
Harada, A.; Takashima, Y.; Yamaguchi, H. *Chem. Soc. Rev.* **2009**, *38*, 875 – 882.

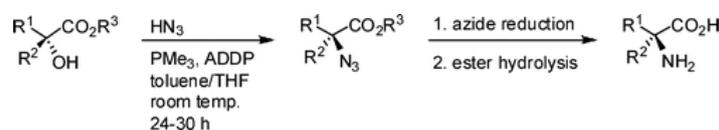
Abstract:



Recently, supramolecular chemistry has been expanding to supramolecular polymer chemistry. The combination of cyclic molecules and linear polymers has provided many kinds of intriguing supramolecular architectures, such as rotaxanes and catenanes. This *tutorial review* overviews construction of some supramolecular architectures formed by cyclodextrins or their derivatives with guest molecules. In the first part, the construction of supramolecular structures of cyclodextrins with some polymers (polyrotaxanes) is described. In the second part, formation of supramolecular oligomers and polymers formed by cyclodextrin derivatives is described.

- Mitsunobu Approach to the Synthesis of Optically Active α,α -Disubstituted Amino Acids
Green, J. E.; Bender, D. M.; Jackson, S.; O'Donnell, M. J.; McCarthy, J. R. *Org. Lett.* **2009**, *11*, 807-810.

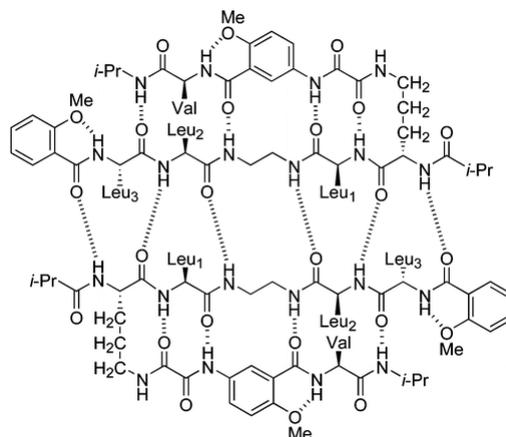
Abstract:



Chiral tertiary α -hydroxy esters of known stereochemical configuration were transformed to α -azido esters by Mitsunobu reaction with HN_3 . Optimization of this reaction was shown to proceed at room temperature with high chemical yield using 1,1-(azodicarbonyl)dipiperidine (ADDP) and trimethylphosphine (PMe_3). Complete inversion of configuration was observed at the α -carbon. Several α,α -disubstituted amino acids were synthesized in high overall chemical yield and optical purity.

- A New Artificial β -Sheet That Dimerizes through Parallel β -Sheet Interactions
Levin, S.; Nowick, J. S. *Org. Lett.* **2009**, *11*, 1003-1006.

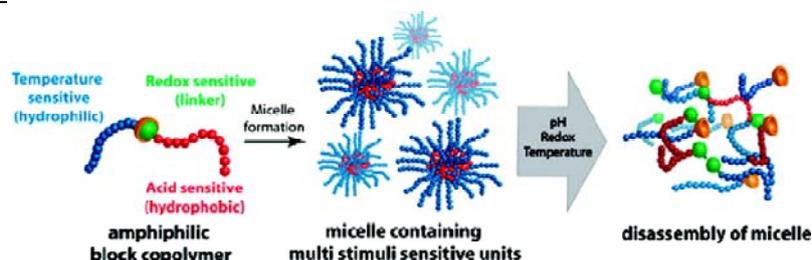
Abstract:



This paper introduces a chemical model of a β -sheet that dimerizes through parallel β -sheet interactions in CDCl_3 solution. The model consists of two C-terminally linked dipeptides connected to a molecular template. ^1H NMR studies establish the β -sheet folding and dimerization of the model system. This system corroborates that linking two peptide strands and blocking one edge of the assembly creates soluble, easy-to-study systems that participate in the types of interactions that occur widely in peptide and protein aggregates.

- Multi-Stimuli Sensitive Amphiphilic Block Copolymer Assemblies
Klaikherd, A.; Nagamani, C.; Thayumanavan, T. *J. Am. Chem. Soc.* **2009**, *131*, 4830–4838.

Abstract:



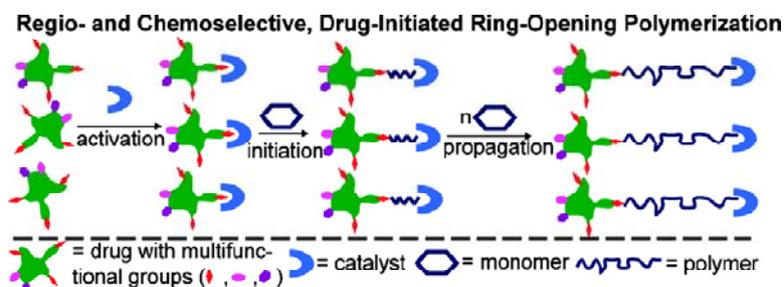
Stimuli-responsive polymers are arguably the most widely considered systems for a variety of applications in biomedical arena. We report here a novel triple stimuli sensitive block copolymer assembly that responds to changes in temperature, pH and redox potential. Our block copolymer design constitutes an acid-sensitive THP-protected HEMA as the hydrophobic part and a temperature-sensitive PNIPAM as the hydrophilic part with an intervening disulfide bond. The micellar properties and the release kinetics of the encapsulated guest molecule in response to one stimulus as well as combinations of stimuli have been evaluated. Responsiveness to combination of

stimuli not only allows for fine-tuning the guest molecule release kinetics, but also provides the possibility of achieving location-specific delivery.

- Ring-Opening Polymerization-Mediated Controlled Formulation of Polylactide–Drug Nanoparticles

Tong, R.; Cheng, J. *J. Am. Chem. Soc.* **2009**, *131*, 4744–4754.

Abstract:



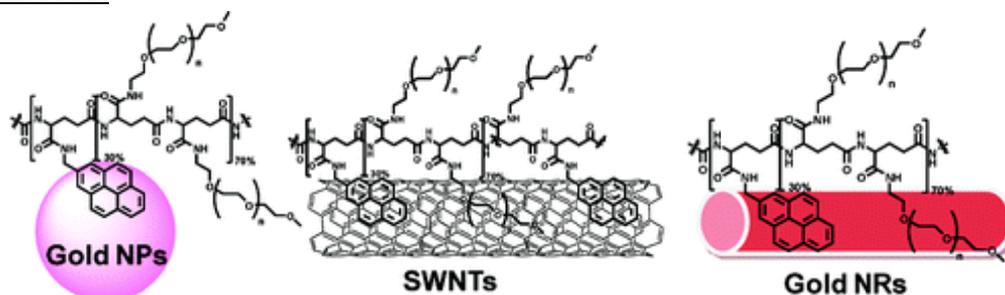
We report here a unique method for formulating doxorubicin-polylactide (Doxo-PLA) conjugate nanoparticles, known as nanoconjugates (NCs), through Doxo/(BDI)ZnN(TMS)₂-mediated [(BDI) 2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)-imino)-2-pentene], chemo- and regioselective polymerizations of lactide (LA) followed by nanoprecipitation. When Doxo/(BDI)ZnN(TMS)₂ was mixed with 1-pyrenemethanol (Pyr-OH) and 1-pyrenemethylamine (Pyr-NH₂) and the mixture was utilized for the polymerization of LA, remarkable chemoselectivity was observed. Pyr-OH was completely consumed and covalently linked to the terminus of the PLA, whereas the Pyr-NH₂ remained intact in the polymerization solution. When Doxo was used as the initiator to polymerize LA in the presence of (BDI)ZnN(TMS)₂, the polymerization was complete within hours, with nearly 100% Doxo-loading efficiency and 100% LA conversion. Doxo loading as high as 27% could be achieved at a LA/Doxo ratio of 10. Both the steric bulk of the chelating ligand and the metal catalyst had dramatic effects on the regioselectivity during the initiation step. When Doxo/(BDI)ZnN(TMS)₂ was mixed with succinic anhydride (SA) to mimic the initiation of Doxo/(BDI)ZnN(TMS)₂-mediated LA polymerization, Doxo-14-succinic ester (Doxo-SE) was the predominate product. When the steric bulk of BDI was reduced or when the BDI ligand was removed, significant amounts of Doxo-4',14-bis-succinic ester (Doxo-2SE) and Doxo-4',9,14-trisuccinic ester (Doxo-3SE) were formed. The use of (BDI)MgN(TMS)₂ in such a reaction also resulted in reduced regioselectivity and formation of both Doxo-SE and Doxo-2SE. Doxo/(BDI)ZnN(TMS)₂-mediated LA polymerizations yielded Doxo-PLA conjugates with well-controlled molecular weights and polydispersities (as low as 1.02). The nanoprecipitation of Doxo-PLA formed NCs less than 150 nm in size with narrow particle size distributions. The sustained release of Doxo from Doxo-PLA NCs was achieved without a burst release. This method may have widespread utility for controlled conjugation of hydroxyl-containing agents to polyesters and formation of corresponding nanoparticles.

- PEG Branched Polymer for Functionalization of Nanomaterials with Ultralong Blood Circulation

Prencipe, G.; Tabakman, S. M.; Welsher, K.; Liu, Z.; Goodwin, A. P.; Zhang, L.; Henry, J.; Dai, H. *J. Am. Chem. Soc.* **2009**, *131*, 4783–4787.

4

Abstract:

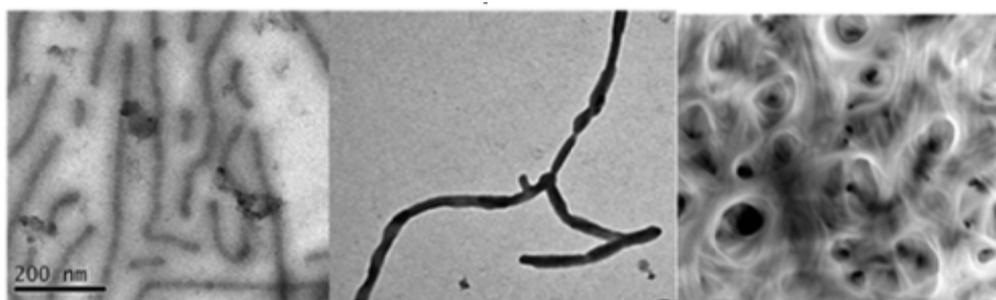


Nanomaterials have been actively pursued for biological and medical applications in recent years. Here, we report the synthesis of several new poly(ethylene glycol) grafted branched polymers for functionalization of various nanomaterials including carbon nanotubes, gold nanoparticles (NPs), and gold nanorods (NRs), affording high aqueous solubility and stability for these materials. We synthesize different surfactant polymers based upon poly(γ -glutamic acid) (γ PGA) and poly(maleic anhydride-*alt*-1-octadecene) (PMHC₁₈). We use the abundant free carboxylic acid groups of γ PGA for attaching lipophilic species such as pyrene or phospholipid, which bind to nanomaterials via robust physisorption. Additionally, the remaining carboxylic acids on γ PGA or the amine-reactive anhydrides of PMHC₁₈ are then PEGylated, providing extended hydrophilic groups, affording polymeric amphiphiles. We show that single-walled carbon nanotubes (SWNTs), Au NPs, and NRs functionalized by the polymers exhibit high stability in aqueous solutions at different pH values, at elevated temperatures, and in serum. Moreover, the polymer-coated SWNTs exhibit remarkably long blood circulation ($t_{1/2} = 22.1$ h) upon intravenous injection into mice, far exceeding the previous record of 5.4 h. The ultralong blood circulation time suggests greatly delayed clearance of nanomaterials by the reticuloendothelial system (RES) of mice, a highly desired property for in vivo applications of nanomaterials, including imaging and drug delivery.

- Self-Assembly of Janus Cylinders into Hierarchical Superstructures

Walther, A.; Drechsler, M.; Rosenfeldt, S.; Harnau, L.; Ballauff, M.; Abetz, V.; Müller, A. H. E. *J. Am. Chem. Soc.* **2009**, *131*, 4720–4728.

Abstract:



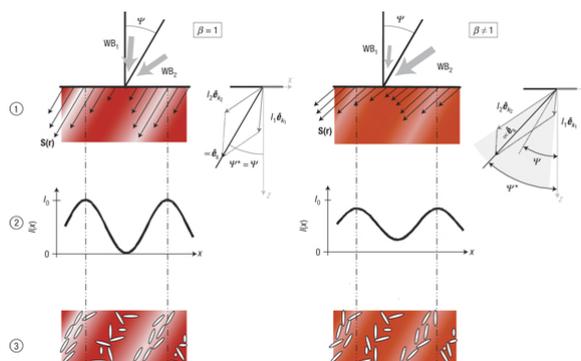
We present in-depth studies of the size tunability and the self-assembly behavior of Janus cylinders possessing a phase segregation into two hemicylinders. The cylinders are prepared by cross-linking the lamella-cylinder morphology of a polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) block terpolymer. The length of the Janus cylinders can be adjusted by both the amplitude and the duration of a sonication treatment from the micro- to the nanometer length. The corona segregation into a biphasic particle is evidenced by selective staining of the PS domains with

RuO₄ and subsequent imaging. The self-assembly behavior of these facial amphiphiles on different length scales is investigated combining dynamic light scattering (DLS), small-angle neutron scattering (SANS), and imaging procedures. Cryogenic transmission electron microscopy images of the Janus cylinders in THF, which is a good solvent for both blocks, exhibit unimolecularly dissolved Janus cylinders with a core–corona structure. These results are corroborated by SANS measurements. Supramolecular aggregation takes place in acetone, which is a nonsolvent for polystyrene, leading to the observation of fiber-like aggregates. The length of these fibers depends on the concentration of the solution. A critical aggregation concentration is found, under which unimolecularly dissolved Janus cylinders exist. The fibers are composed of 2–4 Janus cylinders, shielding the inner insoluble polystyrene hemicylinder against the solvent. Herein, the SANS data reveal a core–shell structure of the aggregates. Upon deposition of the Janus cylinders from more concentrated solution, a second type of superstructure is formed on a significantly larger length scale. The Janus cylinders form fibrillar networks, in which the pore size depends on the concentration and deposition time of the sample.

- Optical gain by a simple photoisomerization process

Gallego-Gómez, F.; del Monte, F.; Meerholz, K. *Nature Materials* **2008**, *7*, 490-497.

Abstract:

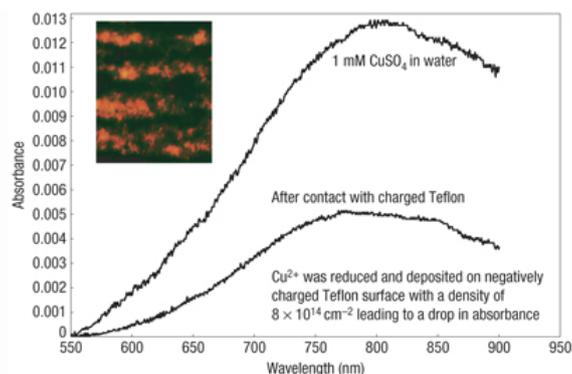


Organic holographic materials are pursued as versatile and cheap data-storage materials. It is generally assumed that under steady-state conditions, only photorefractive holographic media exhibit a non-local response to a light-intensity pattern, which results in an asymmetric two-beam coupling or 'gain', where intensity is transferred from one beam to the other as a measure of writing efficiency. Here, we demonstrate non-local holographic recording in a non-photorefractive material. We demonstrate that reversible photoisomerization gratings recorded in a non-photorefractive azo-based material exhibit large optical gain coefficients beyond $1,000 \text{ cm}^{-1}$, even for polarization gratings. The grating characteristics differ markedly from classical photorefractive features, but can be modelled by considering the influence of the Poynting vector on the photoisomerization. The external control of the Poynting vector enables manipulation of the gain coefficient, including its sign (the direction of energy exchange), a novel phenomenon we refer to as 'gain steering'. A very high sensitivity of about $100 \text{ cm}^2 \text{ J}^{-1}$ was achieved. This high sensitivity, combined with a high spatial resolution, suggests a great technical advantage for applications in image processing and phase conjugation.

- Electrostatic electrochemistry at insulators

Liu, C.; Bard, A. J. *Nature Materials* **2008**, *7*, 505-509.

Abstract:

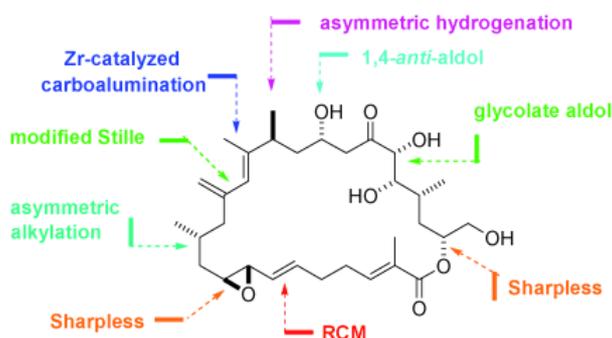


The identity of charges generated by contact electrification on dielectrics has remained unknown for centuries and the precise determination of the charge density is also a long-standing challenge. Here, electrostatic charges on Teflon (polytetrafluoroethylene) produced by rubbing with Lucite (polymethylmethacrylate) were directly identified as electrons rather than ions by electrochemical (redox) experiments with charged Teflon used as a single electrode in solution causing various chemical reactions: pH increases; hydrogen formation; metal deposition; $\text{Fe}(\text{CN})_6^{3-}$ reduction; and chemiluminescence in the system of Teflon(-)/ $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ (analogous to electrogenerated chemiluminescence). Moreover, copper deposition could be amplified by depositing Pd first in a predetermined pattern, followed by electroless deposition to produce Cu lines. This process could be potentially important for microelectronic and other applications because Teflon has desirable properties including a low dielectric constant and good thermal stability. Charge density was determined using Faraday's law and the significance of electron transfer processes on charged polymers and potentially other insulators have been demonstrated.

- Total Syntheses of Amphidinolides B1, B4, G1, H1 and Structure Revision of Amphidinolide H2

Fürstner, A.; Bouchez, L. C.; Morency, L.; Funel, J.-A.; Liepins, V.; Porée, F.-H.; Gilmour, R.; Laurich, D.; Beaufile, F.; Tamiya, M. *Chem. Eur. J.* **2009**, *15*, 3983-4010.

Abstract:



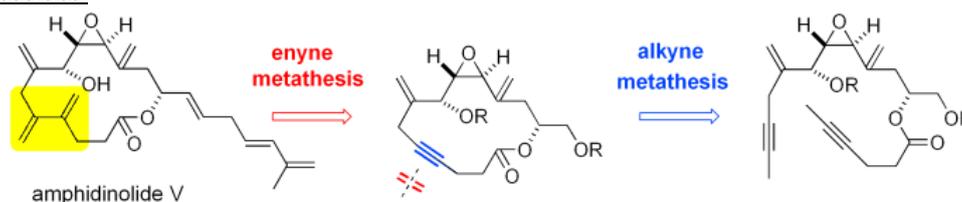
Nature is a pretty unselective "chemist" when it comes to making the highly cytotoxic amphidinolide macrolides of the B/G/H series. To date, 16 different such compounds have been isolated, all of which could now be approached by a highly convergent and largely catalysis-based route (see figure). This notion is exemplified by the total synthesis of five prototype members of this family.

Dinoflagellates of the genus *Amphidinium* produce a "library" of closely related secondary metabolites of mixed polyketide origin, which are extremely scarce but highly promising owing to the exceptional cytotoxicity against various cancer cell lines. Because of the dense array of sensitive functionalities on their largely conserved macrocyclic frame, however, these amphidinolides of the B,

D, G and H types elapsed many previous attempts at their synthesis. Described herein is a robust, convergent and hence general blueprint which allowed not only to conquest five prototype members of these series, but also holds the promise of making “non-natural” analogues available by diverted total synthesis. This notion transpires for a synthesis-driven structure revision of amphidinolide H2. The successful route hinges upon a highly productive Stille-Migita cross-coupling reaction at the congested and chemically labile 1,3-diene site present in all such targets, which required the development of a modified chloride- and fluoride-free protocol. The macrocyclic ring could be formed with high efficiency and selectivity by ring-closing metathesis (RCM) engaging a vinyl epoxide unit as one of the reaction partners. Because of the sensitivity of the targets to oxidizing and reducing conditions as well as to pH changes, the proper adjustment of the protecting group pattern for the peripheral -OH functions also constitutes a critical aspect, which has to converge to silyl groups only once the diene is in place. Tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) turned out to be a sufficiently mild fluoride source to allow for the final deprotection without damaging the precious macrolides.

- Total Synthesis and Biological Evaluation of Amphidinolide V and Analogues
Fürstner, A.; Flügge, S.; Larionov, O.; Takahashi, Y.; Kubota, T.; Kobayashi, J. *Chem. Eur. J.* **2009**, *15*, 4011-4029.

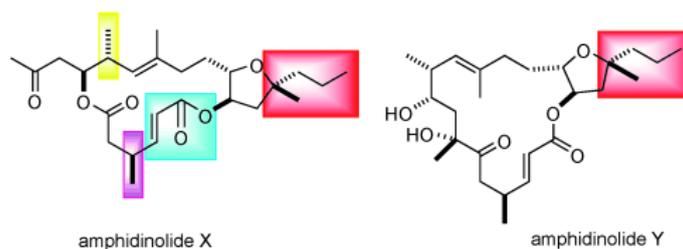
Abstract:



The awesome power of metathesis is illustrated by a concise synthesis of the extremely scarce marine natural product amphidinolide V, which hinges on a sequence of ring-closing alkyne metathesis followed by intermolecular enyne metathesis with ethylene (see scheme). As a complete set of conceivable stereoisomers was prepared, the constitution and absolute configuration of this macrolide could be established and first insights into structure-activity relationships governing its cytotoxicity were obtained.

A sequence of ring-closing alkyne metathesis followed by an intermolecular enyne metathesis of the resulting cycloalkyne with ethene was used to forge the macrocyclic skeleton and to set the vicinal *exo*-methylene branches characteristic for the cytotoxic marine natural product amphidinolide V (**1**). Comparison of the synthetic material with an authentic sample of this extremely scarce metabolite isolated from a dinoflagellate of the *Amphidinium* sp. eliminated any doubts about its structure and allowed the absolute configuration of amphidinolide V to be determined as *8R,9S,10S,13R*. Moreover, the flexibility inherent to the underlying synthesis blueprint also opened access to a comprehensive set of diastereomers of **1** as well as to synthetic analogues differing from the natural lead in the lipophilic chains appended to the macrocyclic core. This set of designed analogues gave first insights into structure-activity relationships, which revealed that the stereostructure of the macrolactone is a highly critical parameter, whereas the examined alterations of the side chain did not diminish the cytotoxicity of the compounds to any notable extent.

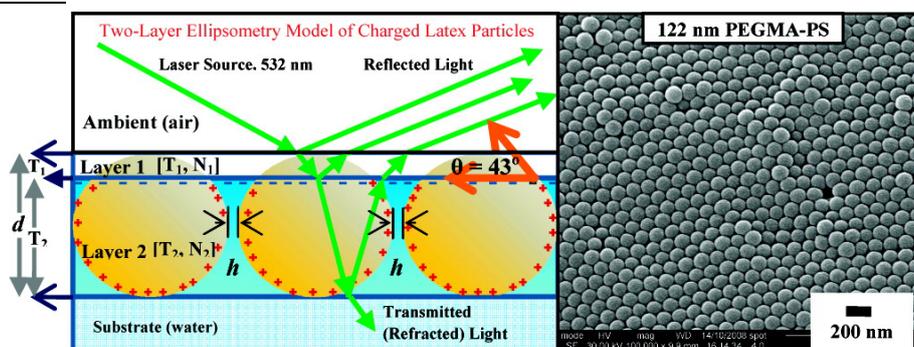
- Molecular Editing and Biological Evaluation of Amphidinolide X and Y
Fürstner, A.; Kattinig, E.; Kelter, G.; Fiebig, H.-H. *Chem. Eur. J.* **2009**, *15*, 4030-4043.

Abstract:

Scarce and precious: A collection of compounds with deep-seated structural “point mutations” within the framework of the marine natural products amphidinolide X and Y was prepared by “diverted total synthesis”. The resulting products provided first insights into the cytotoxicity profile of these extremely scarce macrolides.

Deliberate deviations from the previously described total syntheses of amphidinolide X (**1**) and Y (**2**) allowed a collection of seven designed analogues of these extremely scarce marine natural products to be obtained. These fully synthetic “natural product-like” compounds enabled first insights into the previously unknown structure-activity relationships governing this series. Although the average cytotoxicity is moderate, it was found that certain bladder, colon and prostate cancer cell lines are fairly sensitive, and that the best synthetic analogues are more active than the natural products themselves. The syntheses rely on the 9-MeO-9-BBN variant of the Suzuki coupling for the formation of the carbon frameworks, as well as on Yamaguchi lactonization reactions for the cyclization of the macrocyclic rings.

- Adsorption of Submicrometer-Sized Cationic Sterically Stabilized Polystyrene Latex at the Air#Water Interface: Contact Angle Determination by Ellipsometry
Hunter, T. N.; Jameson, G. J.; Wanless, E. J.; Dupin, D.; Armes, S. P. *Langmuir* **2009**, *25*, 3440-3449.

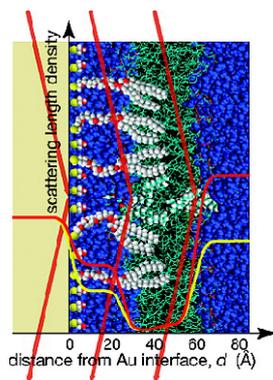
Abstract:

Near-monodisperse, sterically stabilized cationic polystyrene latexes of either 122 or 310 nm diameter were prepared by aqueous emulsion polymerization using cheap, readily available reagents. At low pH, these latexes stabilized foams prepared by either hand-shaking or by using a foam column. SEM studies confirmed that the dried foam mainly comprised well-defined bilayers, which suggests that each air bubble is stabilized with a latex monolayer. Adsorption of the same latexes at the planar air-water interface was studied using the Langmuir-Blodgett trough technique. Surface pressure isotherms confirmed particle desorption from the interface on repeated compression of the latex monolayers. For the 122 nm latex at pH 2, ellipsometric analysis enabled a contact angle of $\sim 43^\circ$ to be calculated from a simple two-layer model, which suggests that these

particles have only moderate wettability. Similar results were obtained for the 310 nm latex, but the data were much less reliable in this case due to additional background particle scattering.

- A New Lipid Anchor for Sparsely Tethered Bilayer Lipid Membranes†
Heinrich, F.; Ng, T.; Vanderah, D. J.; Shekhar, P.; Mihailescu, M.; Nanda, H.; Lösche, M.
Langmuir **2009**, *25*, 4219-4229.

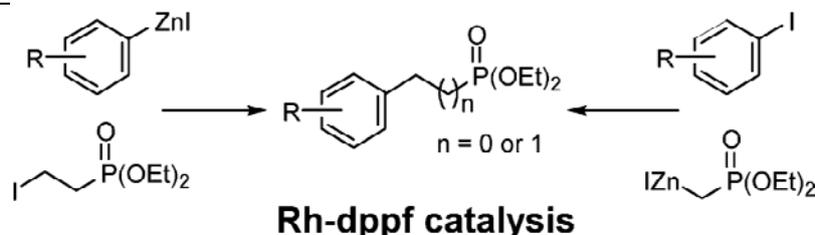
Abstract:



Mixed self-assembled monolayers (SAMs) of ω -mercaptoethanol and the new synthetic lipid 1,2-dipalmityl-3- $[\omega$ -mercaptonona(ethylene oxide)] glycerol (FC16) were investigated for their ability to form sparsely tethered bilayer lipid membranes (stBLMs) completed with various phospholipids. We investigated the structural and functional properties of FC16-based stBLMs and compared these to stBLMs prepared using a previously characterized synthetic lipid, 1,2-dimyristyl-3- $[\omega$ -mercaptohexa(ethylene oxide)] glycerol (WC14). FC16-based stBLMs show increased resistivity to ion transfer and an increase in the submembrane space of ~ 0.5 nm. Importantly, FC16-based stBLMs formed well-defined, complete bilayers with charged phospholipids such as 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphoglycerol (POPG). In these, POPG incorporates into the outer monolayer leaflet in the same ratio as in the immersion solution but is excluded from the inner leaflet. In all cases that we have investigated thus far, the area densities of the lipids within the bilayers were on average close to those in free bilayer membranes. For charged phospholipids, FC16 appears to provide a distinct advantage over WC14 for the formation of well-defined stBLMs.

- Rh-Catalyzed Negishi Alkyl-Aryl Cross-Coupling Leading to α - or β -Phosphoryl-Substituted Alkylarenes
Takahashi, H.; Inagaki, S.; Yoshii, N.; Gao, F.; Nishihara, N.; Takagi, K. *J. Org. Chem.* **2009**, *74*, 2794-2797.

Abstract:



The catalytic cross-coupling between ArZnX and $\text{ICH}_2(\text{CH}_2)_n\text{P}(\text{O})(\text{OEt})_2$ ($n = 0-3$) has been investigated to determine the utility of the Rh catalyst during the alkyl-aryl cross-coupling and to develop a new synthetic method for phosphoryl-substituted alkylarenes. Rh-dppf exhibits an excellent catalytic activity for the reaction with the alkylphosphonate of $n = 1$, whereas for the reaction with those of n

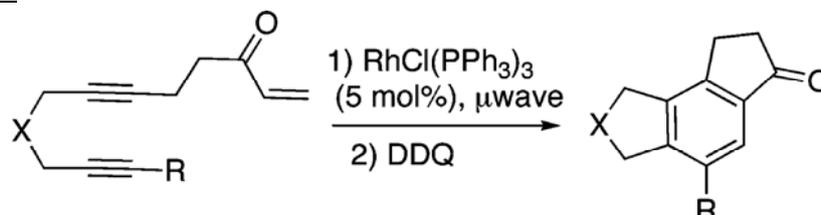
= 2 or 3, β -hydride elimination mainly takes place. As for the reaction with an alkylphosphonate of $n = 0$, a polarity inversion of the coupling components is necessary in order to provide the coupling products; the phosphoryl analogue of the Reformatsky reagent and ArI give the cross-coupling products in good yields through the catalysis by Rh-dppf.

10

- Intramolecular Rhodium-Catalyzed [2+2+2] Cyclizations of Diynes with Enones

Jones, A. L.; Snyder, J. K. *J. Org. Chem.* **2009**, *74*, 2907-2910.

Abstract:

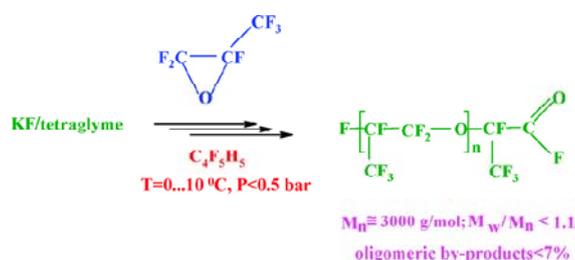


The Rh(I)-catalyzed inter- and intramolecular [2+2+2] cyclization of diynes with R,α -unsaturated enones proceeds with microwave promotion in good yields. This chemistry was applied to the synthesis of (-)-alcyopterosin I.

- Anionic Ring-Opening Polymerization of Hexafluoropropylene Oxide Using Alkali Metal Fluorides as Catalysts: A Mechanistic Study.

Kostjuk, S. V.; Ortega, E.; Ganachaud, F.; Améduri, B.; Boutevin, B. *Macromolecules*, **2009**, *42*, 612-619.

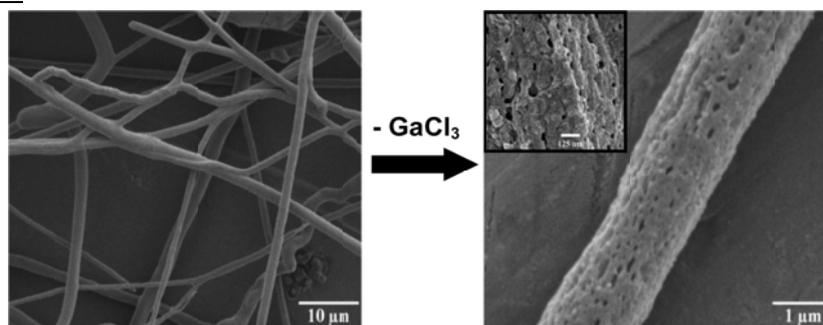
Abstract:



The anionic ring-opening polymerization of hexafluoropropylene oxide using the conventional alkali metal fluorides/tetraglyme catalytic system in the presence of different fluorinated solvents at various temperatures and under batch conditions is reported. Basically, the sodium fluoride (NaF)/tetraglyme system gave only monoadduct $\text{CF}_3\text{CF}_2\text{CO}_2\text{CH}_3$, while cesium fluoride (CsF)/tetraglyme produced oligomeric product with number-average degree of polymerization (DP_n) less than 5. The higher molar mass polymers were synthesized using the potassium fluoride (KF)/tetraglyme catalytic system and 1,1,1,3,3-pentafluorobutane ($\text{C}_4\text{F}_5\text{H}_5$) or 1,3-bis(trifluoromethyl)benzene as solvent at 0 °C. Under these conditions, polymers with number-average molar masses ranging between 2500 and 3500 g mol⁻¹ were obtained in high contents (>90%) and almost without any low molar mass (DP_n ≤ 5) contaminants (4-7%). Polymers which chain ends were derived into methyl esters were fully characterized by gas chromatography, ¹⁹F and ¹H NMR, and MALDI-TOF-MS spectroscopy. A kinetic study allowed us to propose a tentative mechanism entailing (i) the livingness of the polymerization of the hexafluoropropylene oxide with KF/tetraglyme catalytic system and (ii) the importance on the control of molar masses of the biphasic gas/liquid environment in the batch autoclave.

- Porous Nylon-6 Fibers via a Novel Salt-Induced Electrospinning Method.
Gupta, A.; Saqing, C. D.; Afshari, M.; Tonelli, A. E.; Khan, S. A.; Kotek, R. *Macromolecules* **2009**, *42*, 709-715.

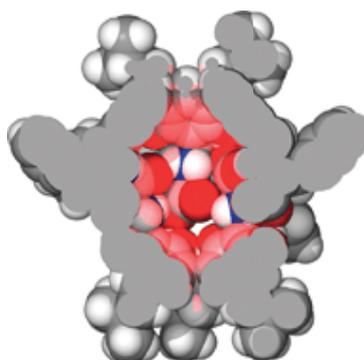
Abstract :



Porous nylon-6 fibers are obtained from Lewis acid-base complexation of gallium trichloride (GaCl_3) and nylon-6 using electrospinning followed by GaCl_3 removal. DSC and FTIR results reveal that the electrospun fibers, prior to GaCl_3 removal, are amorphous with no hydrogen bonds present between nylon-6 chains. GaCl_3 being a Lewis acid interacts with the Lewis base sites (CdO groups) on the nylon-6 chains, thereby preventing the chains to crystallize via intermolecular hydrogen bonding. Subsequent removal of GaCl_3 from the as-spun fibers by soaking the electrospun web in water for 24 h leads to the formation of pores throughout the fibers. While the average fiber diameter remains effectively the same after salt removal, the average surface area increases by more than a factor of 6 for the regenerated fibers. The dual use of a metal salt (Lewis acid) to (a) facilitate fiber formation by temporary removal of polymer interchain interactions and (b) act as a porogen provides a facile approach to obtain porous fibers via electrospinning.

- A self-assembled chiral capsule with polar interior.
Kuberski, B.; Szumna, A. *Chem. Commun.* **2009**, 1959 – 1961.

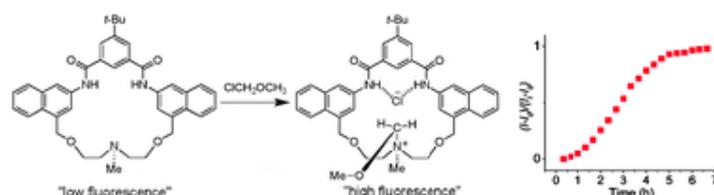
Abstract :



Phenylalanine substituted resorcinarenes form self-complementary dimeric homo- or heterochiral capsules based on deeply buried electrostatic interactions (salt bridges) with numerous polar and non-polar functionalities in their interiors available for interactions with encapsulated polar molecules, as proved by X-ray analysis and diffusion NMR spectroscopy.

- Fluorescent chemosensor for reactive organohalides in micellar solution with an example of autocatalysis.
Lee, J. J.; Smith, B. D. *Chem. Commun.* **2009**, 1962 – 1963.

Abstract :

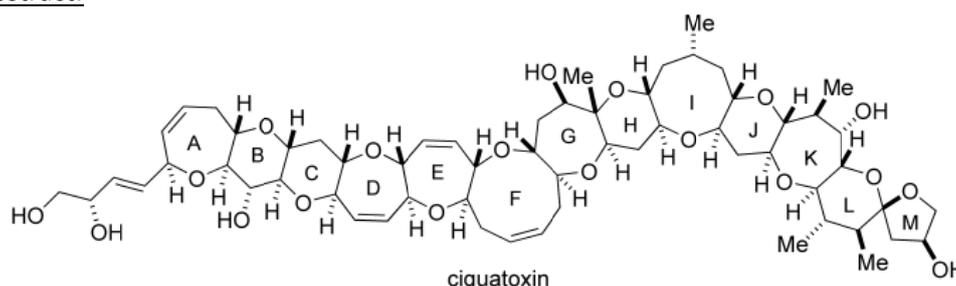


N-Alkylation of a fluorescent macrocyclic amine in aqueous micellar solution produces enhanced emission; the reaction with chloromethyl methyl ether exhibits autocatalysis.

- Total Synthesis of Ciguatoxin

Hamajima, A.; Isobe, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 2941–2945.

Abstract:

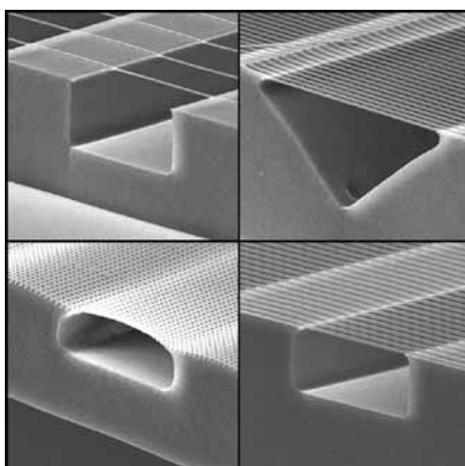


Something fishy: Ciguatoxin (see structure) is one of the principal toxins involved in ciguatera poisoning and the target of a total synthesis involving the coupling of three segments. The key transformations in this synthesis feature acetylene-dicobalthexacarbonyl complexation.

- Fabrication of Monolithic Bridge Structures by Vacuum-Assisted Capillary-Force Lithography

Kwak, R.; Jeong, H. E.; Suh, K. Y. *Small* **2009**, *5*, 790–794.

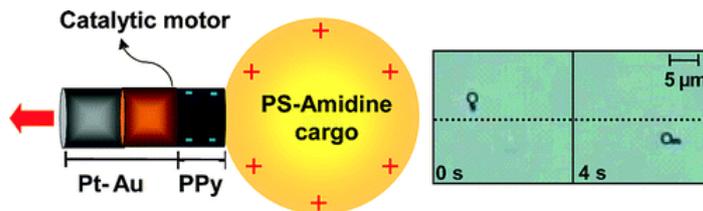
Abstract:



Bridging the gap: Vacuum-assisted capillary force lithography (CFL) allows the fabrication of monolithic, suspended bridge structures (see picture) by exploiting partial curing kinetics and vacuum-assisted hydraulic filling. A small portion of the base microstructure (<4 μm) is molded to create a bridge structure by simply applying a nanoscale mold with the impression of channels, meshes, or circles.

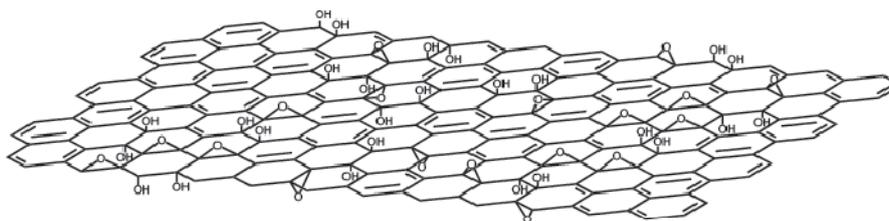
- Catalytic Motors for Transport of Colloidal Cargo

Sundararajan, S.; Lammert, P. E.; Zudans, A; W.; Crespi, V. H.; Sen, A. *Nano Lett.* **2008**, *8*, 1271–1276.

Abstract:

Autonomous micro- and nanomotors should, in principle, deliver materials in a site-directed fashion, powering the assembly of dynamic, nonequilibrium superstructures. Here we demonstrate that catalytic Pt–Au nanomotors can transport a prototypical cargo: polystyrene microspheres. In addition, motors with Ni segments can overcome both Brownian orientational fluctuations and biased rotation of the rod–sphere doublet to enable persistent steerable uniaxial motion in an external magnetic field. Assuming a cargo-independent motive force, the speeds are inversely proportional to the Stokes resistance, which we compute using a completed double-layer boundary integral equation. In addition, we demonstrate motors transporting cargo via chemotaxis toward a H_2O_2 fuel source.

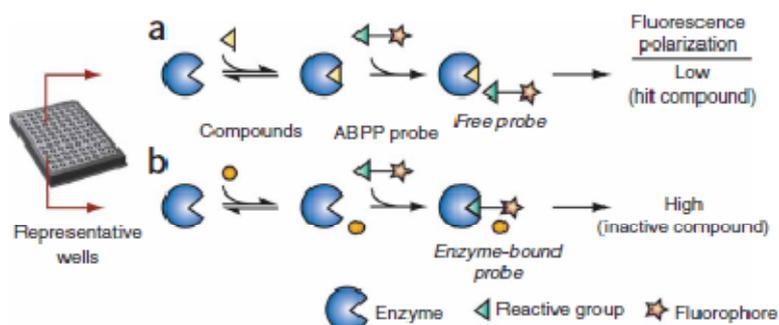
- Chemical methods for the production of graphenes
Park, S.; Ruoff, R. S. *Nature Nanotechnology* **2009**, *4*, 217-224.

Abstract:

Interest in graphene centers on its excellent mechanical, electrical, thermal and optical properties, its very high specific surface area, and our ability to influence these properties through chemical functionalization. There are a number of methods for generating graphene and chemically modified graphene from graphite and derivatives of graphite, each with different advantages and disadvantages. Here we review the use of colloidal suspensions to produce new materials composed of graphene and chemically modified graphene. This approach is both versatile and scalable, and is adaptable to a wide variety of applications.

- Identification of selective inhibitors of uncharacterized enzymes by high-throughput screening with fluorescent activity-based probes
Bachovchin, D. A.; Brown, S. J.; Rosen, H.; Cravatt, B. F. *Nature Biotechnology* **2009**, *27*, 387 – 394.

Abstract:



High-throughput screening to discover small-molecule modulators of enzymes typically relies on highly tailored substrate assays, which are not available for poorly characterized enzymes. Here we report a general, substrate-free method for identifying inhibitors of uncharacterized enzymes. The assay measures changes in the kinetics of covalent active-site labeling with broad-spectrum, fluorescent probes in the presence of inhibitors by monitoring the fluorescence polarization signal. We show that this technology is applicable to enzymes from at least two mechanistic classes, regardless of their degree of functional annotation, and can be coupled with secondary proteomic assays that use competitive activity-based profiling to rapidly determine the specificity of screening hits.

Using this method, we identify the bioactive alkaloid emetine as a selective inhibitor of the uncharacterized cancer-associated hydrolase RBBP9. Furthermore, we show that the detoxification enzyme GSTO1, also implicated in cancer, is inhibited by several electrophilic compounds found in public libraries, some of which display high selectivity for this protein.