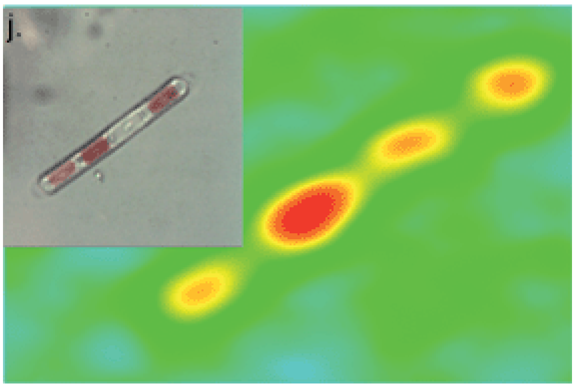
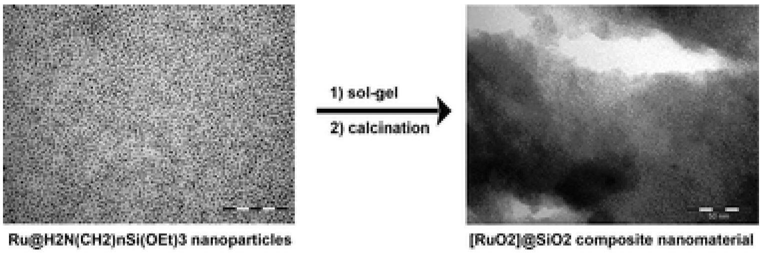
- Nano-gold biosynthesis by silica-encapsulated micro-algae: a “living” bio-hybrid material
  Sicard, C.; Brayner, R.; Margueritat, J.; Hémadi, M.; Couté, A.; Yéprémian, C.; Djediat, C.; Aubard, J.; Fiévet, F.; Livage, J.; Coradin, T. *J. Mater. Chem.* **2010**, *20*, 9342-9347.
  Abstract:



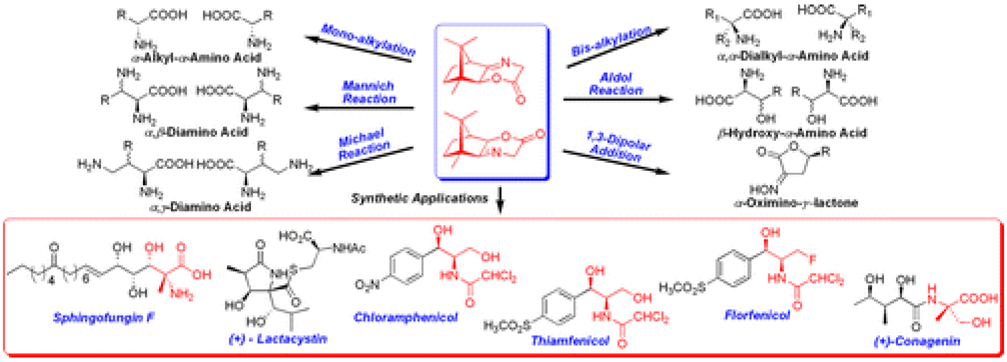
Klebsormidium flaccidum algal cells exhibiting the ability to form gold nanoparticles intra-cellularly in suspension were encapsulated within silica gels. Optical and electronic microscopy indicate that entrapped cells maintain their ability to reduce gold salts. A difference in the kinetics of gold colloid formation within silica in the absence or presence of cells could be followed by UV-visible absorption spectroscopy, confirming the bio-mediated nature of the reduction process. Study of the photosynthetic activity of the algae showed that the encapsulation process protects the cells from lethal effects arising from gold toxicity. Moreover, the first *in situ* imaging of entrapped cells using Raman spectroscopy allowed the investigation of the influence of the gold colloids on the photosynthetic system of the algae, in particular through modification of chlorophyll fluorescence and carotenoid signals. Such a coupling of sol–gel encapsulation and Raman imaging should allow the future development of novel photosynthesis-based cellular biosensors.

- Synthesis of composite ruthenium-containing silica nanomaterials from amine-stabilized ruthenium nanoparticles as elemental bricks
  Tristany, M.; Philippot, K.; Guari, Y.; Collière, V.; Lecante, P.; Chaudret, B. *J. Mater. Chem.* **2010**, *20*, 9523-9530.
  Abstract:



A facile synthesis of composite ruthenium-containing silica nanomaterials from amine stabilized-ruthenium nanoparticles as elemental bricks is described. This route takes advantage of an organometallic approach and the use of bifunctional $H_2N–(CH_2)_x–Si(OEt)_3$ amines as stabilizing ligands (x = 3, 11) for the synthesis of ruthenium nanoparticles, from [Ru(COD)(COT)] (COD = 1,3-cyclooctadiene, COT = 1,3,5-cyclooctatriene) as the metal precursor. Classical hydrolysis and polycondensation steps of the sol–gel approach further lead to the formation of the silica matrix around the ruthenium nanoparticles. $[RuO_2]@SiO_2$ nanocomposites are then obtained through a calcination step in air. The final composite nanomaterials were characterized by different techniques and they were found to possess a high specific surface area making them attractive materials for catalysis.

- Synthesis of α-Amino Acids Based on Chiral Tricycloiminolactone Derived from Natural (+)-Camphor
  Luo, Y.-C.; Zhang, H.-H.; Wang, Y.; Xu, P.-F. *Acc. Chem. Res.* **2010**, *43*, 1317–1330.
  Abstract:



Amino acids are one of the most important classes of the building blocks of life: they are the structural subunits of proteins, peptides, and many secondary metabolites. In addition to the 20 α-amino acids that constitute the backbone of proteins, hundreds of other natural α-amino acids have been discovered either in free form or as components in natural products. The difference between these molecules is the substituents at the chiral carbon situated between the amino and carboxyl moieties; this carbon (and any atom along a chain attached to it) is thus an important synthetic target.

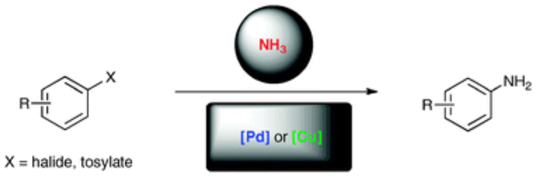
Because tailor-made α-amino acids are increasingly popular in biochemistry and organic synthesis, further refinement in synthetic methods to generate both natural (l-configuration) and unnatural (d-configuration) amino acids is a very active area of current research. In this Account, we examine the tricycloiminolactones, which are versatile glycine equivalents derived from natural camphor. We have developed the tricycloiminolactones in our laboratory and used them in the synthesis of several kinds of enantiopure α-amino acids.

As nucleophiles, enolated tricycloiminolactones were shown to successfully participate in alkylations, Aldol reactions, Michael additions, and Mannich reactions. These reactions all gave excellent stereoselectivities and high yields. Simple conversion of the products offered α-alkyl-α-amino acids, α,α-dialkyl-α-amino acids, β-hydroxy-α-amino acids, α,γ-diamino acids, and α,β-diamino acids. One particular advantage is that the same electrophile can react with two chiral templates in the same way, thus affording access to both enantiomeric amino acids. In other words, some natural (l-configuration) α-amino acids and their unnatural (d-configuration) counterparts can be prepared very conveniently.

The relation between substrate structures and product stereoconformations derived from our investigations serves as a convenient guide in the synthesis of useful chiral amino acids. In addition, highly stereoselective 1,3-diploar cycloadditions between alkenes and chiral nitrones derived from tricycloiminolactones provide a potential method for the synthesis of γ-hydroxy-α-amino acids.

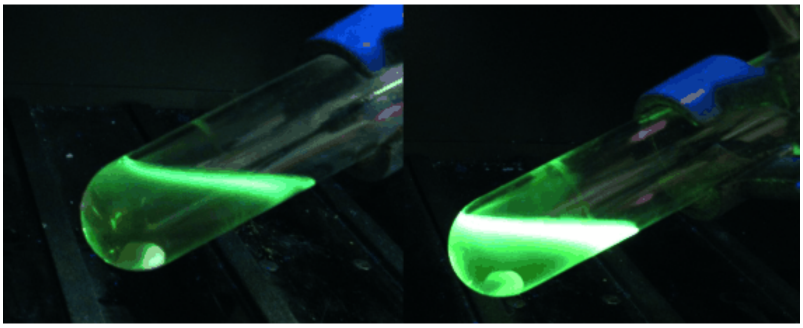
We also discuss applications of our methods in the synthesis of complex natural products, including conagenin, polyoxamic acid, lactacystin, and sphingofungin F. The preparation of some clinically important drug molecules, such as thiaphenicol, florfenicol, and chloramphenicol, was greatly simplified with our methods. The tricycloiminolactones offer a number of advantages in the synthesis of both natural and unnatural α-amino acids and provide many useful building blocks in the synthetic pursuit of complex molecules.

- Direct amination of aryl halides with ammonia
  Aubin, Y.; Fischmeister, C.; Thomas, C. M.; Renaud, J.-L. *Chem. Soc. Rev.* **2010**, *39*, 4130-4145.
  Abstract:



The traditional homogeneous access to aromatic amine derivatives is a nucleophilic aromatic substitution of the corresponding aryl halides. The halogen atom is usually relatively inert to amination reaction unless it is activated by the presence of electron withdrawing groups. Consequently, there has been particular emphasis over the past decade on the synthesis of metal complexes that are active catalysts for the preparation of aromatic amines. This *tutorial review* focuses on the use of metal-based complexes for the direct amination of aryl halides with ammonia.

- How Important Is the Release–Return Mechanism in Olefin Metathesis?
  Vorfalt, T. T.; Wannowius, K. J.; Thiel, V.; Plenio, H. *Chem.-Eur. J.* **2010**, *16*, 12312-12315.
  Abstract:



From whose bourns no traveller returns, puzzles the will: UV/Vis, ^{19}F-NMR, and fluorescence spectroscopic studies (see graphic) provide no evidence supporting the boomerang mechanism in Grubbs–Hoveyda complexes, which is the return of the isopropoxy styrene as a benzylidene ether ligand following its release during catalyst initiation.

- The Dynamic Chemistry of Molecular Borromean Rings and Solomon Knots
  Meyer, C. D.; Forgan, R. S.; Chichak, K. S.; Peters, A. J.; Tangchaivang, N.; Cave, G. W. V.; Khan, S. I.; Cantrill, S. J.; Stoddart, J. F. *Chem.-Eur. J.* **2010**, *16*, 12570-12581.
  Abstract:

CHEMISTRY
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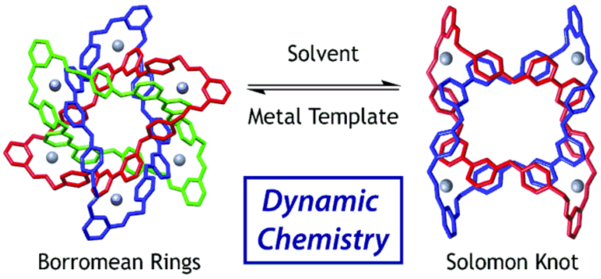
DOI: 10.1002/chem.201001806

The Dynamic Chemistry of Molecular Borromean Rings and Solomon Knots

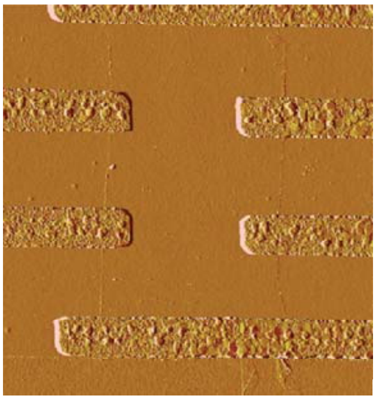
Cari D. Meyer,[a] Ross S. Forgan,[b] Kelly S. Chichak,[a] Andrea J. Peters,[a] Nicholas Tangchaivang,[a] Gareth W. V. Cave,[c] Saeed I. Khan,[a] Stuart J. Cantrill,[a] and J. Fraser Stoddart*[a, b]

12570 View this journal online at wileyonlinelibrary.com © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim *Chem. Eur. J.* **2010**, *16*, 12570 – 12581



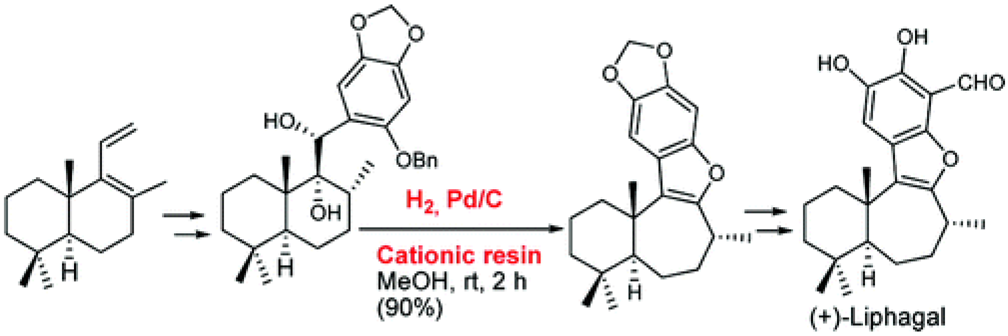
The dynamic solution equilibria between molecular Borromean rings (BRs) and Solomon knots (SKs), assembled from transition metal-templated macrocycles, consisting of *exo*-bidentate bipyridyl and *endo*-tridentate diiminopyridyl ligands, have been examined with respect to the choice of the metal template and reaction conditions employed in the synthesis of the metalated BRs, otherwise known as Borromeates. Three new Borromeates, their syntheses templated by Cu(II), Co(II), and Mn(II), have been characterized extensively (two by X-ray crystallography) to the extent that the metal centers in the assemblies have been shown to be distanced sufficiently from each other not to communicate. The solid-state structure of the Co(II)–Borromeate reveals that six MeOH molecules, arranged in a [OH···O] hydrogen bonded, chair-like conformation, are located within its oxophilic central cavity. When a mixture of CuII and Zn(II) is used as the source of templation, there exists a dynamic equilibrium, in MeOH at room temperature, between a mixed-metal BR and a SK, from which the latter has been fractionally crystallized. By employing appropriate synthetic protocols with Zn(II) or Cd(II) as the template, significant amounts of SKs are formed alongside BRs. Modified crystallization conditions resulted in the isolation of both an all-zinc BR and an all-zinc SK, crystals of which can be separated manually, leading to the full characterization of the all-zinc SK by ^{1}H-NMR spectroscopy and X-ray crystallography. This doubly interlocked [2]catenate has been identified retrospectively in recorded spectra, where it was attributed previously to a Borromeate with a Zn(II) cation coordinated to the oxophilic interior walls of the ensemble. Interestingly, these Zn(II)-templated assemblies do not interconvert in MeOH at room temperature, indicating the significant influence of both the metal template and solvent on the solution equilibria. It would also appear that d^{10} metal ions favor SK formation—no evidence of Cu(II)-, Co(II)-, or Mn(II)-templated SKs has been found, yet a 1:0.9 ratio of BR:SK has been identified by ^{1}H-NMR spectroscopy when Cd(II) is used as the template.

- Boron nitride substrates for high-quality graphene electronics
  Dean, C. R.; Young, A. F.; Meric, I.; Lee, C.; Wang, L.; Sorgenfrei, S.; Watanabe, K.; Taniguchi, T.; Kim, P.; Shepard, K. L.; Hone, J. *Nature Nanotechnology* **2010**, *5*, 722-726.
  <u>Abstract:</u>



Graphene devices on standard SiO_2 substrates are highly disordered, exhibiting characteristics that are far inferior to the expected intrinsic properties of graphene. Although suspending the graphene above the substrate leads to a substantial improvement in device quality, this geometry imposes severe limitations on device architecture and functionality. There is a growing need, therefore, to identify dielectrics that allow a substrate-supported geometry while retaining the quality achieved with a suspended sample. Hexagonal boron nitride (h-BN) is an appealing substrate, because it has an atomically smooth surface that is relatively free of dangling bonds and charge traps. It also has a lattice constant similar to that of graphite, and has large optical phonon modes and a large electrical bandgap. Here we report the fabrication and characterization of high-quality exfoliated mono- and bilayer graphene devices on single-crystal h-BN substrates, by using a mechanical transfer process. Graphene devices on h-BN substrates have mobilities and carrier inhomogeneities that are almost an order of magnitude better than devices on SiO_2. These devices also show reduced roughness, intrinsic doping and chemical reactivity. The ability to assemble crystalline layered materials in a controlled way permits the fabrication of graphene devices on other promising dielectrics and allows for the realization of more complex graphene heterostructures.

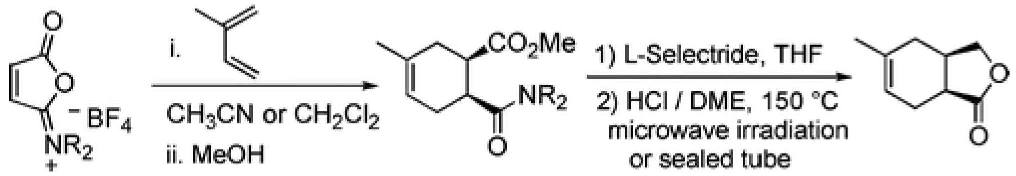
- Enantioselective Total Synthesis of the Selective PI3 Kinase Inhibitor Liphagal
  Alvarez-Manzaneda, E.; Chahboun, R.; Alvarez, E.; Cano, M. J.; Haidour, A.; Alvarez-Manzaneda, R. *Org. Lett.* **2010**, *12*, 4450-4453.
  Abstract:



The enantioselective total synthesis of liphagal, a selective inhibitor of PI3K r isolated from the marine sponge *Aka coralliphaga*, has been achieved. The novel tetracyclic "liphagane" skeleton is formed in one step, after the hydrogenation of a dihydroxydrimane phenol benzyl ether in the presence of cationic resin.

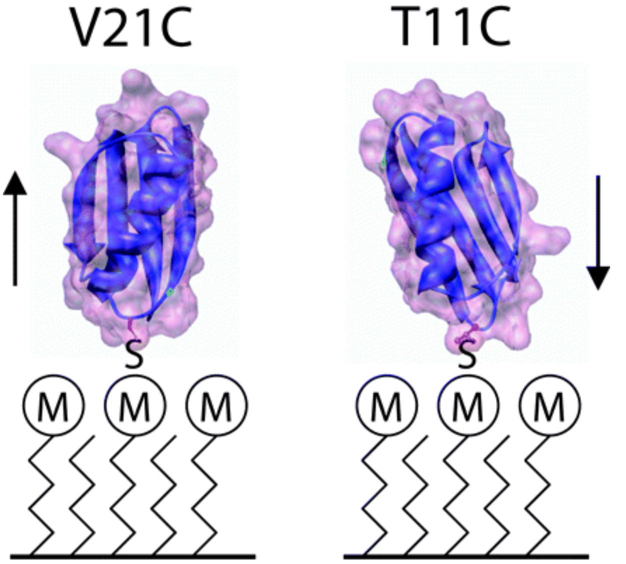
- Diels-Alder Reactions of Cyclic Isoimidium Salts
  Boeckman, Jr., R. K.; Miller, Y.; Ryder, T. R. *Org. Lett.* **2010**, *12*, 4524-4527.

Abstract:



Diels-Alder reactions of cyclic isoimidium salts are described. The corresponding cycloadducts are obtained with high regio- and stereoselectivity. The use of homochiral cyclic isoimidium salts delivers cycloadducts with excellent diastereoselectivity (>99:1) that can be efficiently converted to enantiomerically pure lactones.

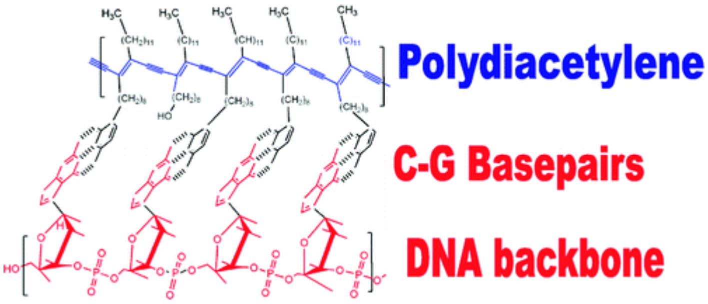
- Probing the Orientation of Surface-Immobilized Protein G B1 Using ToF-SIMS, Sum Frequency Generation, and NEXAFS Spectroscopy
  Baugh, L.; Weidner, T.; Baio, J. E.; Nguyen, P.-C. T.; Gamble, L. J.; Stayton, P. S.; Castner, D. G.
  Langmuir **2010**, *26,* 16434–16441.
  Abstract:



The ability to orient active proteins on surfaces is a critical aspect of many medical technologies. An important related challenge is characterizing protein orientation in these surface films. This study uses a combination of time-of-flight secondary ion mass spectrometry (ToF-SIMS), sum frequency generation (SFG) vibrational spectroscopy, and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to characterize the orientation of surface-immobilized Protein G B1, a rigid 6 kDa domain that binds the Fc fragment of IgG. Two Protein G B1 variants with a single cysteine introduced at either end were immobilized via the cysteine thiol onto maleimide-oligo(ethylene glycol)-functionalized gold and bare gold substrates. X-ray photoelectron spectroscopy was used to measure the amount of immobilized protein, and ToF-SIMS was used to measure the amino acid composition of the exposed surface of the protein films and to confirm covalent attachment of protein thiol to the substrate maleimide groups. SFG and NEXAFS were used to characterize the ordering and orientation of peptide or side chain bonds. On both substrates and for both cysteine positions, ToF-SIMS data showed enrichment of mass peaks from amino acids located at the end of the protein opposite to the cysteine surface position as compared with nonspecifically immobilized protein, indicating end-on protein orientations. Orientation on the maleimide substrate was enhanced by increasing pH (7.0−9.5) and salt concentration (0−1.5 M NaCl). SFG spectral peaks

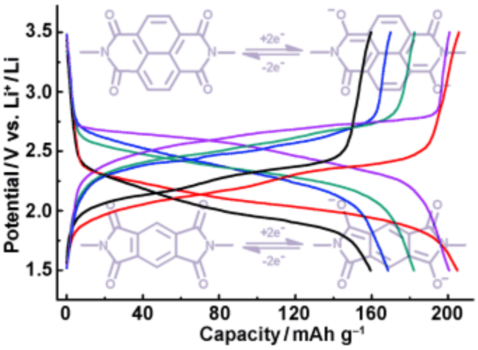
characteristic of ordered α-helix and β-sheet elements were observed for both variants but not for cysteine-free wild type protein on the maleimide surface. The phase of the α-helix and β-sheet peaks indicated a predominantly upright orientation for both variants, consistent with an end-on protein binding configuration. Polarization dependence of the NEXAFS signal from the N 1s to π* transition of β-sheet peptide bonds also indicated protein ordering, with an estimated tilt angle of inner β-strands of 40−50° for both variants (one variant more tilted than the other), consistent with SFG results. The combined results demonstrate the power of using complementary techniques to probe protein orientation on surfaces.

- Enantioselective Recognition between Polydiacetylene Nucleolipid Monolayers and Complementary Oligonucleotides
  Sigal-Batikoff, I.; Konovalov, O.; Singh, A.; Berman, A. *Langmuir* **2010**, *26*, 16424-16433.
  Abstract:



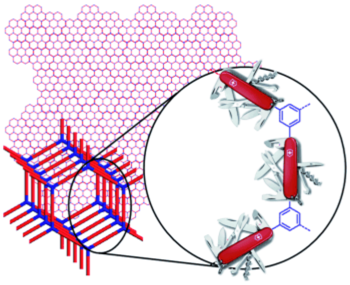
A two-dimensional bio/synthetic hybrid system at the air−solution interface made of a polymerized diacetylene Langmuir film with nucleobase modified headgroups is presented. The polymerized film presents a crystalline array of nucleobases, capable of specific binding of complementary mononucleoside or oligonucleotide sequences. Mixed monolayers of the linear polyconjugated polydiacetylene (PDA) films derivatized with cytosine (10,12-pentacosadiyne-cytidyl, PDC) monomers and alcohol-terminated diacetylene lipid (10,12-pentacosadiynol, PDOH) at a 3:1 ratio (PDC 75%) were compressed and polymerized at the air−water interface with circular polarized light (CPL) or nonpolarized UV light. Here we report a grazing incidence X-ray diffraction (GIXD) investigation of PDC films polymerized to different chirality and hybridized with complementary ssDNA strands. We have demonstrated enantioselective interactions on synthetic structured interfaces produced by Langmuir surface compression followed by polymerization with circular polarized UV light (CPL). The *left*- and *right*-CPL polymerized light exhibit the same well-defined crystalline structure. The observed difference between *left*- and *right*-CPL polymerized PDC 75% Langmuir films compressed over the complementary mononucleotide guanosine or hybridized with fully complementary ss$G_{12}T_5$ oligonucleotide in the subphase suggests that they are indeed enantiomeric structures, capable of enantioselective binding of their natural ligand, guanosine, solely as a result of surface induced asymmetry in "*left*" but not in "*right*" form. This observation may also be related to the intriguing question of chiral selection during the early period of "Origin of Life". We show that achiral compounds, as a result of irradiation with circular polarized light, can organize in chiral surface structures capable of amplification of biopolymer binding of particular handedness.

- Polyimides: Promising Energy-Storage Materials
  Song, Z.; Zhan, H.; Zhou, Y. *Angew. Chem. Int. Ed.* **2010**, *49*, 8444-8448.
  Abstract:



Plastic batteries: Polyimides are proposed as cathode materials for rechargeable lithium batteries. Although they are regarded as insulators, five polyimides with different structures all show good electrochemical activity and some of them show promising performance, which could allow their use in a new generation of "green battery" applications.

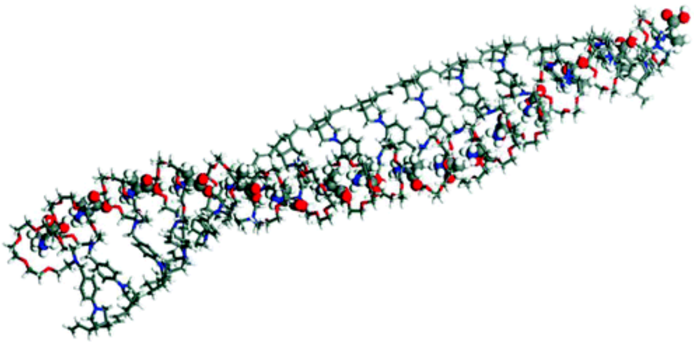
- Functional Materials: From Hard to Soft Porous Frameworks
  Thomas, A. *Angew. Chem. Int. Ed.* **2010**, *49*, 8328-8344.
  Abstract:



Functional Porous Frameworks

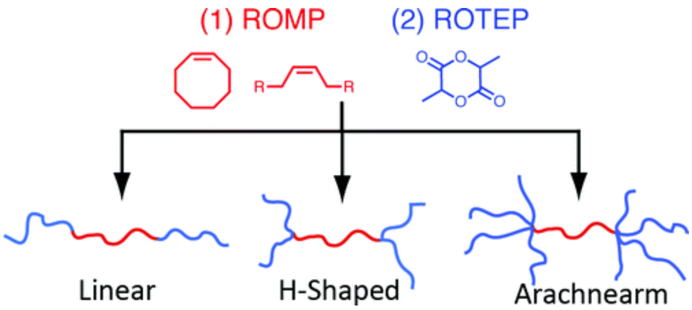
This Review aims to give an overview of recent research in the area of porous, organic–inorganic and purely organic, functional materials. Possibilities for introducing organic groups that exhibit chemical and/or physical functions into porous materials will be described, with a focus on the incorporation of such functional groups as a supporting part of the pore walls. The number of organic groups in the network can be increased such that porous, purely organic materials are obtained.

- Protonated Amino Acid-Induced One-Handed Helicity of Polynorbornene Having Monoaza-18-crown-6 Pendants
  Ji, R.; Chao, C.-G.; Huang, Y.-C.; Lan, Y.-k.; Lu, C.-L.; Luh, T.-Y. *Macromolecules* **2010**, *43*, 8813–8820.
  Abstract:



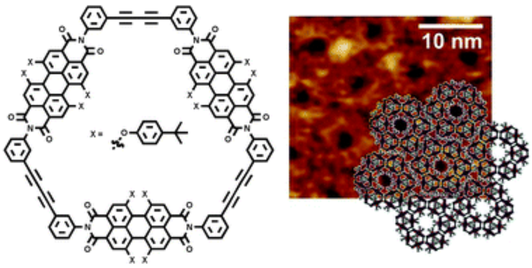
Upon complexation with protonated amino acids, one-handed helical polynorbornenes appended with monoaza-18-crown-6 (**7a**) are obtained. The cooperativity is observed as revealed by the sergeant–soldier effect and the majority rule. When sterically hindered amino acids such as phenylalanine, isovaline or proline, esters of amino acids, and aminoalcohols are used, the Δε values in CD spectra are significantly reduced. The protonated ammonium ion may form complex with a crown ether moiety whereas the carboxylic acid may form hydrogen bonding with the adjacent crown ether pendant resulting in unidirectional orientation of the pendants leading to a helical scaffold. The corresponding dimer **10** with the same isotactic stereochemistry as that of polynorbornene **7a** behaves similarly to exhibit bisignate CD curve upon treatment with protonated alanine. On the other hand, polynorbornene with monoaza-15-crown-5 (**7b**) does not exhibit any CD response under the same conditions.

- Synthesis of Linear, H-Shaped, and Arachnearm Block Copolymers By Tandem Ring-Opening Polymerizations
  Pitet, L. M.; Chamberlain, B. M.; Hauser, A. W.; Hillmyer, M. A. *Macromolecules* 2010, 43, 8018–8025.
  Abstract:



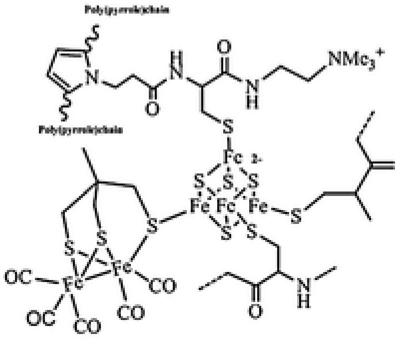
We have demonstrated the two-stage preparation of block polymers with various architectures containing mechanistically incompatible monomers. Three new monounsaturated chain transfer agents (CTAs) were synthesized containing two, four, or eight hydroxyl groups and used for the preparation of telechelic poly(*cis*-cyclooctene) (PCOE) by ring-opening metathesis polymerization (ROMP). We observed excellent end-group fidelity along with well-controlled molecular weights based on the initial monomer to CTA ratio. Each PCOE was subsequently used as a macroinitiator for the polymerization of d,l-lactide to produce compositionally controlled B_xAB_x block polymers with linear (x = 1), H-shaped (x = 2), and arachne(spider)arm (x = 4) architectures. Block polymers were prepared containing PLA weight fractions (w_L) ranging from 0.25–0.85. This report significantly expands on the method of combining mechanistically incompatible monomers via tandem polymerizations by introducing branched architectures that can facilitate specific property tailoring.

- Perylene bisimide macrocycles and their self-assembly on HOPG surfaces
  Schlosser, F.; Stepanenko, V.; Würthner, F. *Chem. Commun.* **2010**, *46*, 8350-8352.
  Abstract:



Acetylene-linked macrocycles incorporating multiple perylene tetracarboxylic acid bisimide (PBI) chromophores have been synthesised and separated by recycling GPC. The very first example of such macrocycles, i.e., cyclic trimer 5, containing three PBI dyes self-assembles into highly ordered donut-shaped unique hexagonal nanopatterns on HOPG surfaces as revealed by atomic force microscopy (AFM).

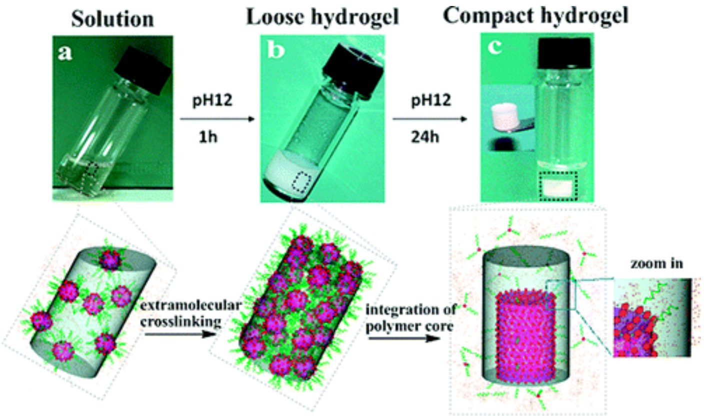
- Artificial hydrogenases: assembly of an H-cluster analogue within a functionalised poly(pyrrole) matrix
  Ibrahim, S.; Woi, P. M.; Alias, Y.; Pickett, C. J. *Chem. Commun.* **2010**, *46*, 8189-8191.
  Abstract:



ν(CO) = 2035,1971, and 1911

We show that a redox active $\{Fe_4S_4\}^{2+}$–cubane assembly covalently bound within a cysteinyl–alkylammonium functionalized polypyrrole can be modified with a diiron dithiolate carbonyl unit to give an artificial hydrogenase H-cluster framework confined within the polymer matrix.

- 'Living' Controlled in Situ Gelling Systems: Thiol−Disulfide Exchange Method toward Tailor-Made Biodegradable Hydrogels
  Wu, D.; Loh, X.; Wu, Y.; Lay, C.; Liu, Y. *J. Am. Chem. Soc.* **2010**, *132*, 15140–15143.
  Abstract:

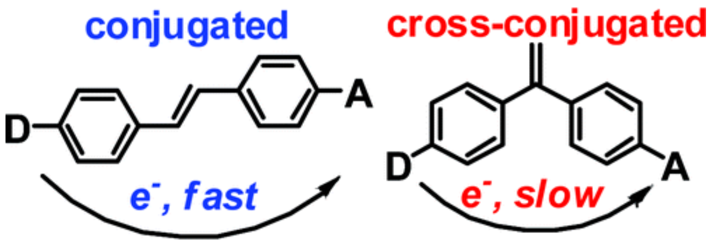


A 'living' controlled hydrogel formation method was first reported to create loose and compact in situ biodegradable hydrogels. The method executed under mild reaction conditions can conveniently tailor the hydrogel properties, and it has the potential to develop into a powerful tool for the design, synthesis, and self-assembly of novel tailor-made biomaterials and drug delivery systems.

- Controlling Electron Transfer in Donor−Bridge−Acceptor Molecules Using Cross-Conjugated Bridges

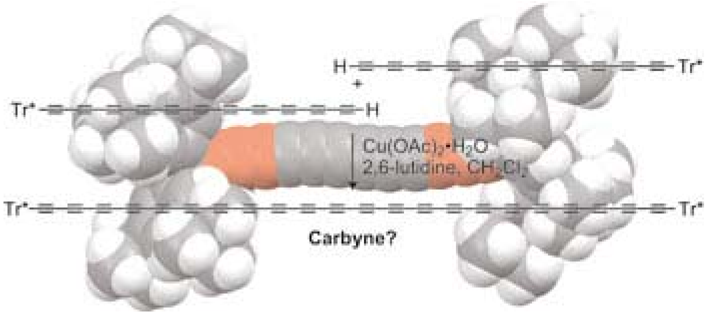
Ricks, A. B.; Solomon, G. C.; Colvin, M. T.; Scott, A. M.; Chen, K.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.*, **2010**, *132*, 15427–15434.

Abstract:



Photoinitiated charge separation (CS) and recombination (CR) in a series of donor−bridge−acceptor (D−B−A) molecules with cross-conjugated, linearly conjugated, and saturated bridges have been compared and contrasted using time-resolved spectroscopy. The photoexcited charge transfer state of 3,5-dimethyl-4-(9-anthracenyl)julolidine (DMJ−An) is the donor, and naphthalene-1,8:4,5-bis(dicarboximide) (NI) is the acceptor in all cases, along with 1,1-diphenylethene, trans-stilbene, diphenylmethane, and xanthone bridges. Photoinitiated CS through the cross-conjugated 1,1-diphenylethene bridge is about 30 times slower than through its linearly conjugated trans-stilbene counterpart and is comparable to that observed through the diphenylmethane bridge. This result implies that cross-conjugation strongly decreases the π orbital contribution to the donor−acceptor electronic coupling so that electron transfer most likely uses the bridge σ system as its primary CS pathway. In contrast, the CS rate through the cross-conjugated xanthone bridge is comparable to that observed through the linearly conjugated trans-stilbene bridge. Molecular conductance calculations on these bridges show that cross-conjugation results in quantum interference effects that greatly alter the through-bridge donor−acceptor electronic coupling as a function of charge injection energy. These calculations display trends that agree well with the observed trends in the electron transfer rates.

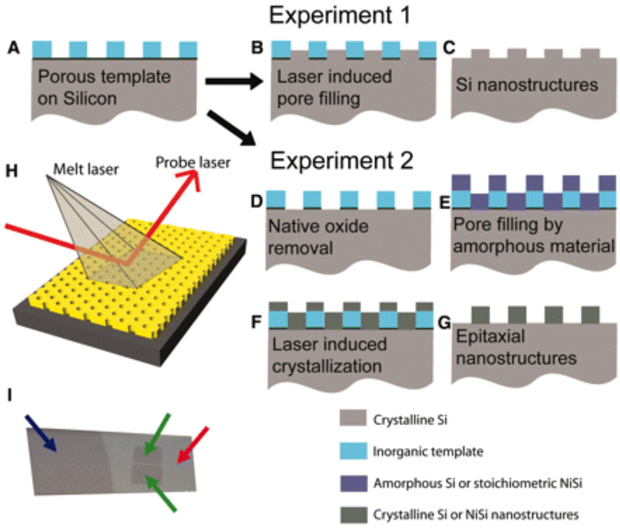
- Synthesis of polyynes to model the *sp*-carbon allotrope carbine
  Chalifoux, W. A.; Tykwinski, R. R. *Nature Chemistry* **2010**, *2*, 967–971.
  Abstract:



Carbyne is an allotrope of carbon composed of *sp*-hybridized carbon atoms. Although its formation in the laboratory is suggested, no well-defined sample is described. Interest in carbyne and its potential properties remains intense because of, at least in part, technological breakthroughs offered by other carbon allotropes, such as fullerenes, carbon nanotubes and graphene. Here, we describe the synthesis of a series of conjugated polyynes as models for carbyne. The longest of the series consists of 44 contiguous acetylenic carbons, and it maintains a framework clearly composed of alternating single and triple bonds. Spectroscopic analyses for these polyynes reveal a distinct trend towards a finite gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital for carbyne, which is estimated to be �485 nm (�2.56 eV). Even the longest members of this

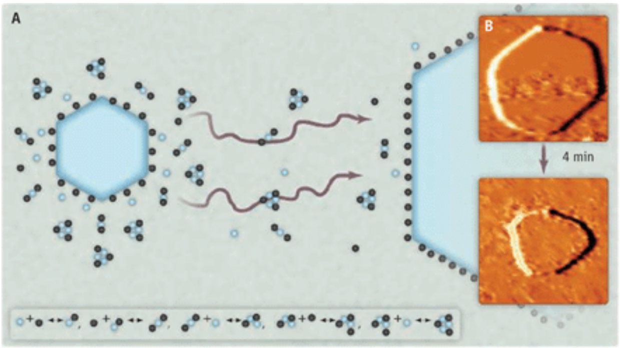
series of polyynes are not particularly sensitive to light, moisture or oxygen, and they can be handled and characterized under normal laboratory conditions.

- Block Copolymer Self-Assembly–Directed Single-Crystal Homo- and Heteroepitaxial Nanostructures
  Arora, H.; Du, P.; Tan, K. W.; Hyun, J. K.; Grazul, J.; Xin, H. L.; Muller, D. A.; Thompson, M. O.; Wiesner, U. *Science* **2010**, *330*, 214 – 219.
  Abstract:



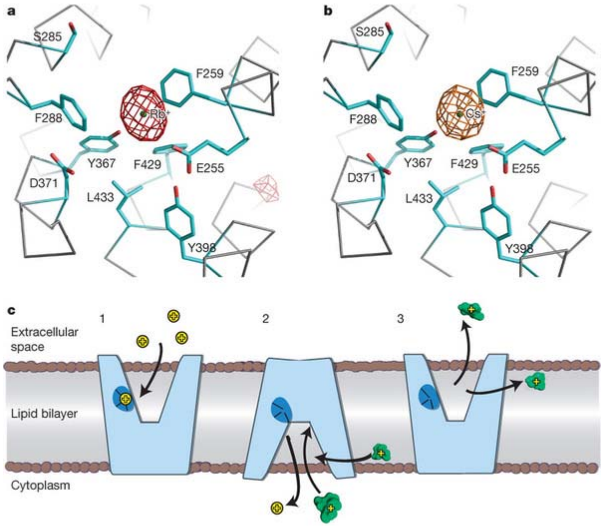
Epitaxy is a widely used method to grow high-quality crystals. One of the key challenges in the field of inorganic solids is the development of epitaxial single-crystal nanostructures. We describe their formation from block copolymer self-assembly–directed nanoporous templates on single-crystal Si backfilled with Si or NiSi through a laser-induced transient melt process. Depending on thickness, template removal leaves either an array of nanopillars or porous nanostructures behind. For stoichiometric NiSi deposition, the template pores provide confinement, enabling heteroepitaxial growth. Irradiation through a mask provides access to hierarchically structured materials. These results on etchable and non-etchable materials suggest a general strategy for growing epitaxial single-crystal nanostructured thin films for fundamental studies and a wide variety of applications, including energy conversion and storage.

- A Little Chemistry Helps the Big Get Bigger
  Evans, J. W.; Thiel, P. A. *Science* **2010**, *330*, 599 – 600.
  Abstract:



What is the common denominator between the geologic formation of gemstones, the degradation of pharmaceutical suspensions, and the manufacture of structural steels? They all can involve a process called coarsening, in which a group of objects of different sizes transforms into fewer objects with larger average size (*1*), such that "the big get bigger." The atoms that occupy boundary locations between different phases tend to be less energetically stable, and coarsening stabilizes the overall system by decreasing the number of such atoms. A fundamental scientific question in coarsening is identifying how the requisite transport of atoms occurs. New answers to this question are being revealed by studies of nanoscale particles that are grown on surfaces.

- Structure of a cation-bound multidrug and toxic compound extrusion transporter
  He, X.; Szewczyk, P.; Karyakin, A.; Evin, M.; Hong, W.-X.; Zhang, Q.; Chang, G. *Nature* **2010**, *467*, 991–994.
  Abstract:



Transporter proteins from the MATE (multidrug and toxic compound extrusion) family are vital in metabolite transport in plants, directly affecting crop yields worldwide. MATE transporters also mediate multiple-drug resistance (MDR) in bacteria and mammals, modulating the efficacy of many pharmaceutical drugs used in the treatment of a variety of diseases. MATE transporters couple substrate transport to electrochemical gradients and are the only remaining class of MDR transporters whose structure has not been determined. Here we report the X-ray structure of the MATE transporter NorM from *Vibrio cholerae* determined to 3.65 Å, revealing an outward-facing conformation with two portals open to the outer leaflet of the membrane and a unique topology of the predicted 12 transmembrane helices distinct from any other known MDR transporter. We also report a cation-binding site in close proximity to residues previously deemed critical for transport. This conformation probably represents a stage of the transport cycle with high affinity for monovalent cations and low affinity for substrates.