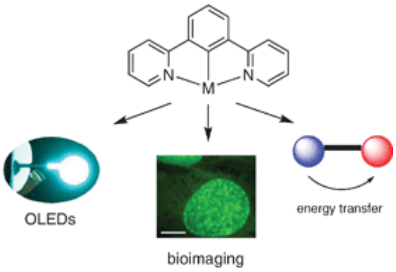
- The coordination chemistry of dipyridylbenzene: N-deficient terpyridine or panacea for brightly luminescent metal complexes?
  Williams, J. A. G. *Chem. Soc. Rev.* **2009**, *38*, 1783 – 1801.
  Abstract:



1,3-Di(2-pyridyl)benzene (dpybH) structurally resembles the widely-used ligand terpyridine (tpy), with which it is isoelectronic. In this *critical review*, following a brief overview of synthetic strategies for dpybH and derivatives, we survey the different types of complex that are possible with these ligands. Whilst metals such as ruthenium(II), osmium(II) and platinum(II) give a terdentate $N^\wedge C^\wedge N$ binding mode in which cyclometallation occurs at C^2, the ions iridium(III), rhodium(III) and palladium(II) favour C^4 metallation. The latter process can be blocked by appropriate ligand modification, to allow the $N^\wedge C^\wedge N$ mode to be accessed with these metal ions too. The luminescence properties of the complexes are discussed. A huge range of emission efficiencies are encountered amongst Ir(III) complexes containing dpyb derivatives, according to the other ligands present. Trends can be rationalised with the aid of simple frontier-orbital considerations. The Pt(II) complexes of dipyridylbenzenes are also intensely luminescent. Their application to contemporary organic light-emitting device (OLED) technology is discussed, including white light emitters exploiting excimer emission. Their potential as cell imaging agents amenable to time-resolved detection procedures on the microsecond timescale has also been demonstrated (118 references).

- Molecular Gastronomy, a Scientific Look at Cooking
  This, H. *Acc. Chem. Res.*, **2009**, *42* (5), pp 575–583
  Abstract:

Food preparation is such a routine activity that we often do not question the process. For example, why do we cook as we do? Why do we eat certain foods and avoid other perfectly edible ingredients? To help answer these questions, it is extremely important to study the chemical changes that food undergoes during preparation; even simply cutting a vegetable can lead to enzymatic reactions.

For many years, these molecular transformations were neglected by the food science field. In 1988, the scientific discipline called “molecular gastronomy” was created, and the field is now developing in many countries. Its many applications fall into two categories. First, there are technology applications for restaurants, for homes, or even for the food industry. In particular, molecular gastronomy has led to “molecular cooking”, a way of food preparation that uses “new” tools, ingredients, and methods. According to a British culinary magazine, the three “top chefs” of the world employ elements of molecular cooking. Second, there are educational applications of molecular gastronomy: new insights into the culinary processes have led to new culinary curricula for chefs in many countries such as France, Canada, Italy, and Finland, as well as educational programs in schools.

In this Account, we focus on science, explain why molecular gastronomy had to be created, and consider its tools, concepts, and results. Within the field, conceptual tools have been developed in order to make the necessary studies. The emphasis is on two important parts of recipes: culinary definitions (describing the objective of recipes) and culinary “precisions” (information that includes old wives’ tales, methods, tips, and proverbs, for example). As for any science, the main objective of molecular gastronomy is, of course, the discovery of new phenomena and new mechanisms. This explains why culinary precisions are so important: cooks of the past could see, but not interpret, phenomena that awaited scientific studies. For French cuisine alone, more than 25 000 culinary precisions have been collected since 1980.

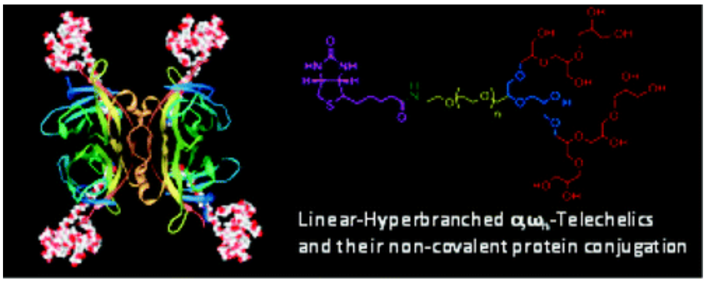
The study of the organization of dishes was improved by the introduction of a formalism called “complex disperse systems/nonperiodical organization of space” (CDS/NPOS). CDS describes the colloidal materials from which the parts of a dish are made; NPOS provides an overall description of a dish. This formalism has proven useful for the study of both scientific (examining phenomena to arrive at a mechanism) and technological (using the results of science to improve technique) applications. For example, it can be used to describe the physical structure of dishes (science) but also to examine the characteristics of classical French sauces (technology).

Many questions still remain in the field of molecular gastronomy. For example, one “Holy Grail” of the field is the prediction of physical, biological, chemical, and organoleptic properties of systems from their CDS/NPOS formula. Another issue to be worked out is the relationship between compound migration in food and chemical modifications of those migrating compounds. These questions will likely keep scientists busy in the near future.

- Synthesis and Noncovalent Protein Conjugation of Linear-Hyperbranched PEG-Poly(glycerol) α,ω_n-Telechelics

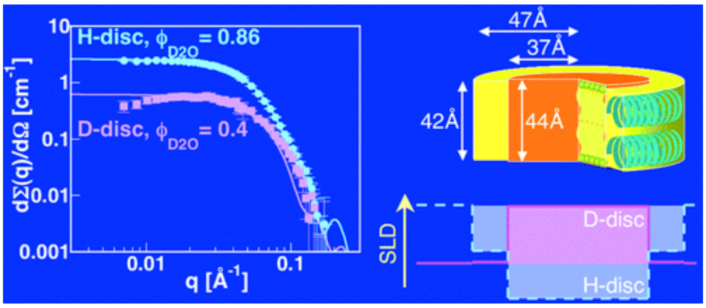
  Wurm, F.; Klos, J. Räder, H. J.; Frey, H. *J. Am. Chem. Soc.* **2009**, *131*, 7954–7955.

  Abstract:



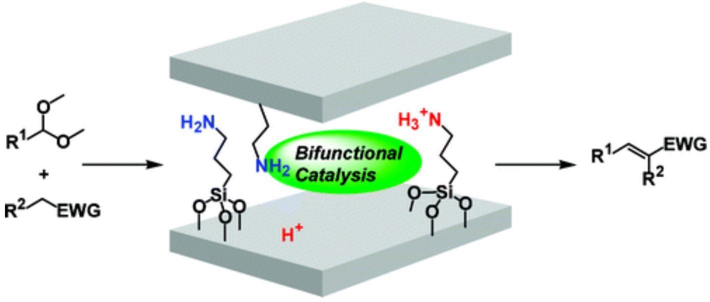
Linear-hyperbranched, heterobifunctional α,ωn telechelic block copolymers consisting of a linear poly(ethylene glycol) (PEG) chain and a hyperbranched polyglycerol (PG) block have been prepared in five steps, using a protected amino-functional initiator. The polyfunctionality ωn (OH groups) can be adjusted by the degree of polymerization (DPn) of the polyglycerol block. Subsequent introduction of a single biotin unit by amidation in α-position permitted noncovalent bioconjugation with avidin.

- Static and Dynamic Properties of Phospholipid Bilayer Nanodiscs
  Nakano, M.; Fukuda, M.; Kudo, T.; Miyazak, M.; Wada, Y.; Matsuzaki, N.; Endo, H.; Handa, T. *J. Am. Chem. Soc.* **2009**, *131*, 8308–8312.
  Abstract:



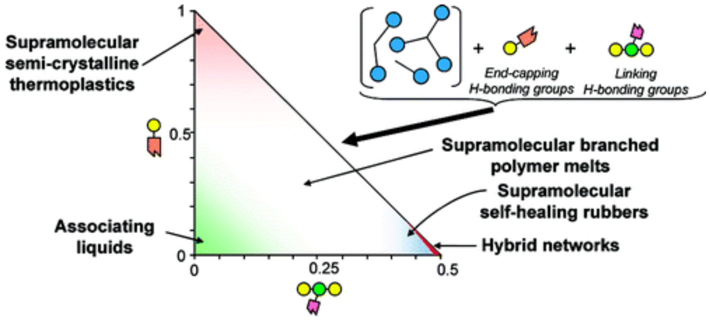
Nanodiscs are phospholipid−protein complexes which are relevant to nascent high-density lipoprotein and are applicable as a drug carrier and a tool to immobilize membrane proteins. We evaluated the structure and dynamics of the nanoparticles consisting of dimyristoylphosphatidylcholine (DMPC) and apolipoprotein A-I (apoA-I) with small-angle neutron scattering (SANS) and fluorescence methods and compared them with static/dynamic properties for large unilamellar vesicles. SANS revealed that the nanodisc includes a lipid bilayer with a thickness of 44 Å and a radius of 37 Å, in which each lipid occupies a smaller area than the reported molecular area of DMPC in vesicles. Fluorescence measurements suggested that DMPC possesses a lower entropy in nanodiscs than in vesicles, because apoA-I molecules, which surround the bilayer, force closer lipid packing, but allow water penetration to the acyl chain ends. Time-resolved SANS experiments revealed that nanodiscs represent a 20-fold higher lipid transfer via an entropically favorable process. The results put forward a conjunction of static/dynamic properties of nanodiscs, where the entropic constraints are responsible for the accelerated desorption of lipids.

- Layered Materials with Coexisting Acidic and Basic Sites for Catalytic One-Pot Reaction Sequences
  Motokura, K.; Tada, M.; Iwasawa, Y. *J. Am. Chem. Soc.* **2009**, *131*, 7944–7945.
  Abstract:



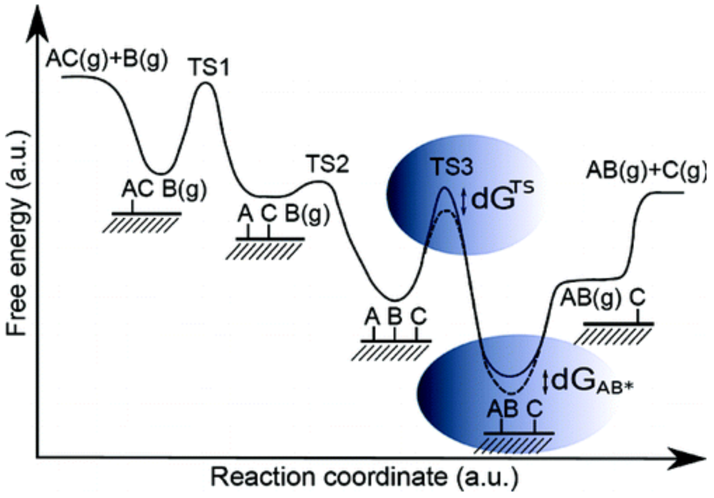
Acidic montmorillonite-immobilized primary amines (H-mont-NH_2) were found to be excellent acid−base bifunctional catalysts for one-pot reaction sequences, which are the first materials with coexisting acid and base sites active for acid–base tamdem reactions. For example, tandem deacetalization-Knoevenagel condensation proceeded successfully with the H-mont-NH_2, affording the corresponding condensation product in a quantitative yield. The acidity of the H-mont-NH_2 was strongly influenced by the preparation solvent, and the base-catalyzed reactions were enhanced by interlayer acid sites.

- Versatile One-Pot Synthesis of Supramolecular Plastics and Self-Healing Rubbers
  Montarnal, D.; Tournilhac, F.; Hidalgo, M.; Couturier, J.-L.; Leibler, L. *J. Am. Chem. Soc.* **2009**, *131*, 7966–7967.
  <u>Abstract:</u>



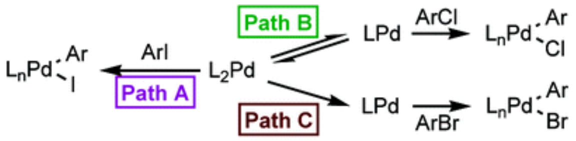
We propose a strategy to obtain through a facile one-pot synthesis a large variety of supramolecular materials that can behave as differently as associating low-viscosity liquids, semicrystalline or amorphous thermoplastics, viscoelastic melts or rubbers. Such versatility is achieved thanks to simultaneous synthesis of branched backbones and grafting of associating units. This contrasts with usual synthetic pathways that rely on grafting functional groups on preprepared backbones. We use oligocondensation of fatty di- and triacids with diethylenetriamine and finely tune the molecular weight and degree of branching by end-capping some acid groups before condensation by reaction with aminoethylimidazolidone. Supramolecular assembly is formed thanks to complementary and self-complementary associations of amide, imidazolidone, and dialkylurea groups, and the stoichiometry directly controls the mesoscopic structure and properties.

- Degree of Rate Control: How Much the Energies of Intermediates and Transition States Control Rates
  Stegelmann, C.; Andreasen, A.; Campbell, C. T. *J. Am. Chem. Soc.* **2009**, *131*, 8077–8082.
  <u>Abstract:</u>



For many decades, the concept of a “rate-determining step” has been of central importance in understanding chemical kinetics in multistep reaction mechanisms and using that understanding to advantage. Yet a rigorous method for identifying the rate-determining step in a reaction mechanism was only recently introduced, via the “degree of rate control” of elementary steps. By extending that idea, we argue that even more useful than identifying the rate-determining step is identifying the rate-controlling transition states and the rate-controlling intermediates. These identify a few distinct chemical species whose relative energies we could adjust to achieve a faster or slower net reaction rate. Their relative energies could be adjusted by a variety of practical approaches, such as adding or modifying a catalyst, modifying the solvent, or simply modifying a reactant’s molecular structure to affect electronic or steric control on the relative energies of the key species. Since these key species are the ones whose relative energies most strongly influence the net reaction rate, they also identify the species whose energetics must be most accurately measured or calculated to achieve an accurate kinetic model for any reaction mechanism. Thus, it is very important to identify these rate-controlling transition states and rate-controlling intermediates for both applied and basic research. Here, we present a method for doing that.

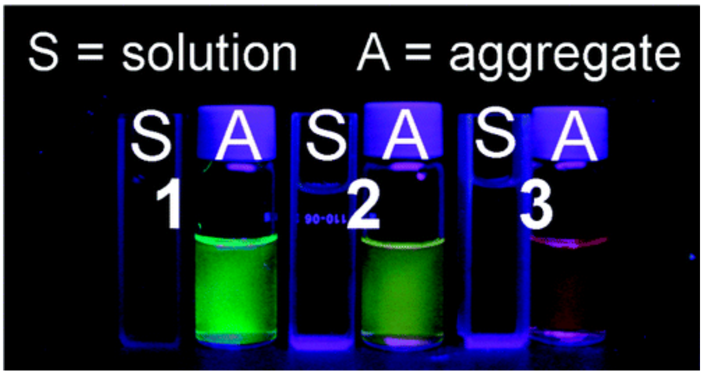
- Effect of Ligand Steric Properties and Halide Identity on the Mechanism for Oxidative Addition of Haloarenes to Trialkylphosphine Pd(0) Complexes
  Barrios-Landeros, F.; Carrow, B. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 8141–8154.
  Abstract:



Partitioning between Paths A, B, and C depends more on the halide than on L
(for L =P^tBu_3, 1-AdP^tBu_2, CyP^tBu_2, PCy_3)

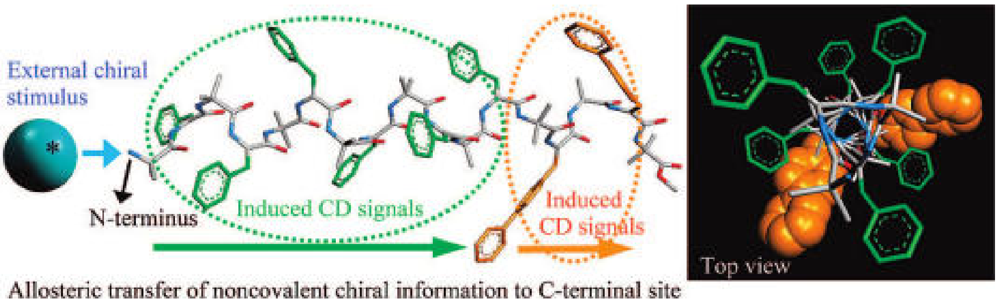
The oxidative addition of PhX (X = I, Br, Cl) to the complexes $Pd(P^tBu_3)_2$ (**1**), Pd(1-Ad$P^tBu_2)_2$ (**2**), Pd(Cy$P^tBu_2)_2$ (**3**), and $Pd(PCy_3)_2$ (**4**) (1-Ad = 1-adamantyl, Cy = cyclohexyl) was studied to determine the effect of steric properties on the coordination number of the species that undergoes oxidative addition and to determine whether the type of halide affects the identity of this species. The kinetic data imply that the number of phosphines coordinated to the complex that reacts in the irreversible step of the oxidative addition process for complexes **1**–**4** depends more on the halide than on the steric properties of the ligands. The rate-limiting step of the oxidative addition of PhI occurred with $L_2Pd(0)$ in all cases, as determined by the lack of dependence of k_{obs} on [P^tBu_3], [1-AdP^tBu_2], or [CyP^tBu_2] and the inverse dependence of the rate constant on [PCy_3] when the reaction was initiated with $Pd(PCy_3)_3$. The irreversible step of the oxidative addition of PhCl occurred with a monophosphine species in each case, as signaled by an inverse dependence of the rate constant on the concentration of ligand. The irreversible step of the oxidative addition of PhBr occurred with a bisphosphine species, as signaled by the zeroth-order or small dependence of the rate constant on the concentration of phosphine. Thus, the additions of the less reactive chloroarenes occur through lower-coordinate intermediates than additions of the more reactive haloarenes.

- Salicylaldehyde Azines as Fluorophores of Aggregation-Induced Emission Enhancement Characteristics
  Tang, W.; Xiang, Y.; Tong, A. *J. Org. Chem.* **2009**, *74*, 2163–2166.
  Abstract :



A series of salicylaldehyde azine derivatives were found to exhibit interesting aggregation-induced emission enhancement (AIEE) characteristics. In good solvent, all these compounds displayed very weak fluorescence, while strong emission was observed when they were placed in poor solvent. Moreover, the AIEE color of these compounds varied from green to red depending on the substituents on azines. Their *in situ* formation also promises potential applications in fluorescence sensing of hydrazine.

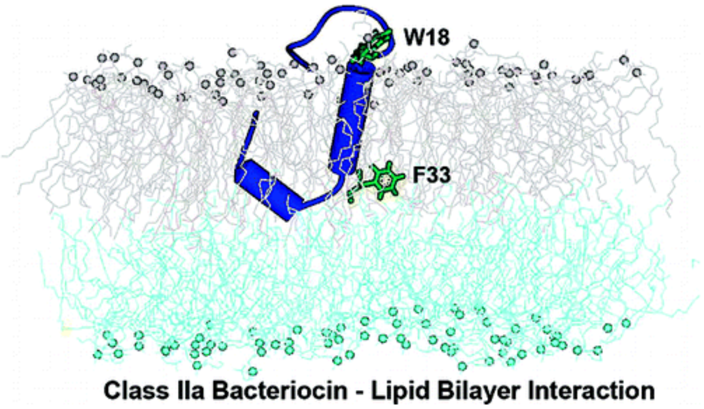
- Transfer of Noncovalent Chiral Information along an Optically Inactive Helical Peptide Chain: Allosteric Control of Asymmetry of the C-Terminal Site by External Molecule that Binds to the N-Terminal Site
  Ousaka, N.; Inai, Y. *J. Org. Chem.* **2009**, *74*, 1429–1439.
  <u>Abstract:</u>



Allosteric transfer of noncovalent chiral information to C-terminal site

This study aims at demonstrating end-to-end transfer of noncovalent chiral information along a peptide chain. The domino-type induction of helical sense is proven by using achiral peptides **1**-*m* of bis-chromophoric sequence with different chain lengths: $\text{H-(Aib-}\Delta^{Z}\text{Phe)}_{m}\text{-(Aib-}\Delta^{Z}\text{Bip)}_{2}\text{-Aib-OCH}_{3}$ [*m* = 2, 4, and 6; Aib = α-aminoisobutyric acid; Δ^{Z}Phe = (*Z*)-α,β-didehydrophenylalanine; Δ^{Z}Bip = (*Z*)-β-(4,4′-biphenyl)-α,β-didehydroalanine]. They all showed the tendency to adopt a 3_{10}-helix. Whereas peptide **1**-*m* originally shows no circular dichroism (CD) signals, marked CD signals were induced at around 270–320 nm based on both the β-aryl didehydroresidues by chiral Boc-proline (Boc = *tert*-butoxycarbonyl). The observed CD spectra were interpreted on the basis of the exciton chirality method and theoretical CD simulation of several helical conformations that were energy-minimized. The experimental and theoretical CD analysis reveals that Boc-L-proline induces the preference for a right-handed helicity in the whole chain of **1**-*m*. Such noncovalent chiral induction was not observed in the corresponding N-terminally protected **1**-*m*. Obviously, helicity induction in **1**-*m* originates from the binding of Boc-proline to the N-terminal site. In the 17-mer (**1**-*6*), the information of helix sense reaches the 16th residue from the N-terminus. We have monitored precise transfer of noncovalent chiral stimulus along a helical peptide chain. The present study also proposes a primitive allosteric model of a single protein-mimicking backbone. Here chiral molecule binding the N-terminal site of **1**-*6* controls the chiroptical signals and helical sense of the C-terminal site about 30 Å away.

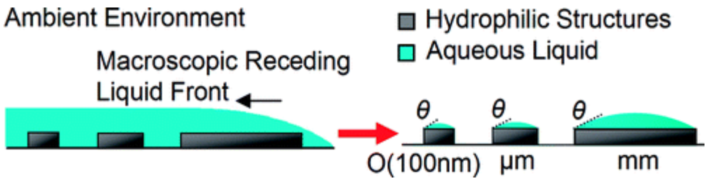
- Interaction of an Antimicrobial Peptide with a Model Lipid Bilayer Using Molecular Dynamics Simulation
  Soliman, W.; Bhattacharjee, S.; Kaur, K. *Langmuir* **2009**, *25*, 6591–6595.
  Abstract:



We present results of molecular dynamics simulations of the interaction of a positively charged antimicrobial peptide, carnobacteriocin B2, with a mixed (anionic-zwitterionic) lipid bilayer carrying a net negative charge. When the peptide is initially immersed in an aqueousmedium, it approaches the bilayer surface because of electrostatic attraction. Insertion of the single peptide in the bilayer, however, is not spontaneous. Simulations are also conducted by employing initial configurations where the peptide is partially or completely inserted into the bilayer. When the peptide is partially inserted into the bilayer, it experiences a slight loss of helical structure with the appearance of a hinge region in the C-terminal helix.

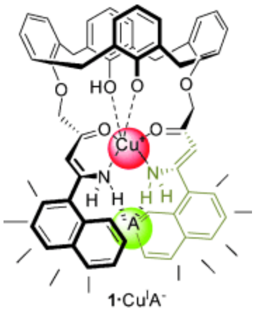
Complete insertion of the peptide in the bilayer results in a stable straight helix with the N- and C-terminals electrostatically tethered to the opposing headgroups of the bilayer. The charged amino acids of the peptide do not cross the charged headgroups of the bilayer in any of the simulations, nor is any bilayer disruption observed in these studies. These results show that single peptides do not spontaneously penetrate lipid membranes and corroborate deductions from previous experimental studies that alternate mechanisms are necessary for their penetration into lipid bilayers.

- Wetting Behaviors of Individual Nanostructures
  Wong, T.-S.; Po-Hao Huang, A.; Ho, C.-M. *Langmuir* **2009**, *25*, 6599–6603.
  Abstract :



Pinning of a liquid contact line by micro/nanoscale defects is attributed as the physical origin of macroscopic contact angle hysteresis. However, direct experimental quantification of the pinning effect at the nanoscale has yet to be fully explored to establish this link. Here we present an experimental technique to systematically investigate the wetting behaviors of individual hydrophilic nanostructures with diameters from 2000 nm down to 75 nm. Our results show that the macroscopic pinning behavior is preserved for nanostructures with dimensions down to ∼200 nm. In addition, the estimated depinning liquid contact angle at the nanoscale is in agreement with the macroscopic receding contact angle, which indicates a physical link between nanoscopic pinning to the macroscopic liquid receding phenomenon.

- Cooperative Recognition of a Copper Cation and Anion by a Calix[4]arene Substituted at the Lower Rim by a β-Amino-α,β-Unsaturated Ketone
  Senthilvelan, A.; Ho, I.-T.; Chang, K.-C.; Lee, G.-H.; Liu, Y.-H.; Chung, W.-S. *Chem. Eur. J.* **2009**, *15*, 6152-6160.
  Abstract:

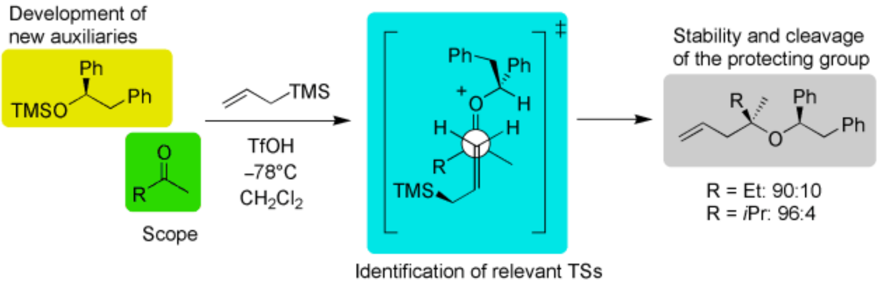


1·Cu^{I}A^{-}

Chemodosimeter: Upon titration with Cu^{II}, the fluorescence of **1** showed strong fluorescence enhancement because the metal ion helps to lock the conformation of the fluorophores. Cu^{II} was reduced to Cu^{I} by the free phenolic OH group of **1**, the phenol was then oxidised by Cu^{II} and assisted in the trapping of Cu^{I}. Ditopic behaviour was observed for **1** ·Cu^{I}, which showed further enhancement of its fluorescence intensity upon complexation with anions (as depicted, A^{-}=CH$_3$COO^{-} or F^{-}).

We report herein a new ditopic calix[4]arene receptor 25,27-bis-{[4-amino-4-(1-naphthyl)-2-oxo-3-butenyl]oxy}-26,28-dihydroxycalix[4]arene (**2**) for the simultaneous complexation of anionic and cationic species. The host molecule 25,27-bis{[3-(1-naphthyl)-5-isoxazolyl]methoxy}-26,28-dihydroxycalix[4]arene (**1**) was synthesised first and was followed by a [Mo(CO)$_6$]-mediated ring-opening reaction to give the target receptor **2**. The binding properties of ligands **1** and **2** towards metal ions in CH$_3$CN were investigated by UV/Vis and fluorescence spectroscopies. The results showed that both ligands **1** and **2** were highly selective for Cu^{II} ions. Upon titration with Cu^{II}, the fluorescence of **1** was severely quenched, whereas **2** showed strong fluorescence enhancement because the metal ions help to lock the conformation of the fluorophores. During the complexation of **2** with Cu^{II}, the Cu^{II} was reduced to Cu^{I} by the free phenolic OH of **2**, whereas the phenol was oxidised by Cu^{II}, after which it assisted in the trapping of Cu^{I}. Ditopic behaviour was observed for the complex **2** ·Cu^{I}, which showed further enhancement of its fluorescence intensity upon complexation with anions such as acetate or fluoride.

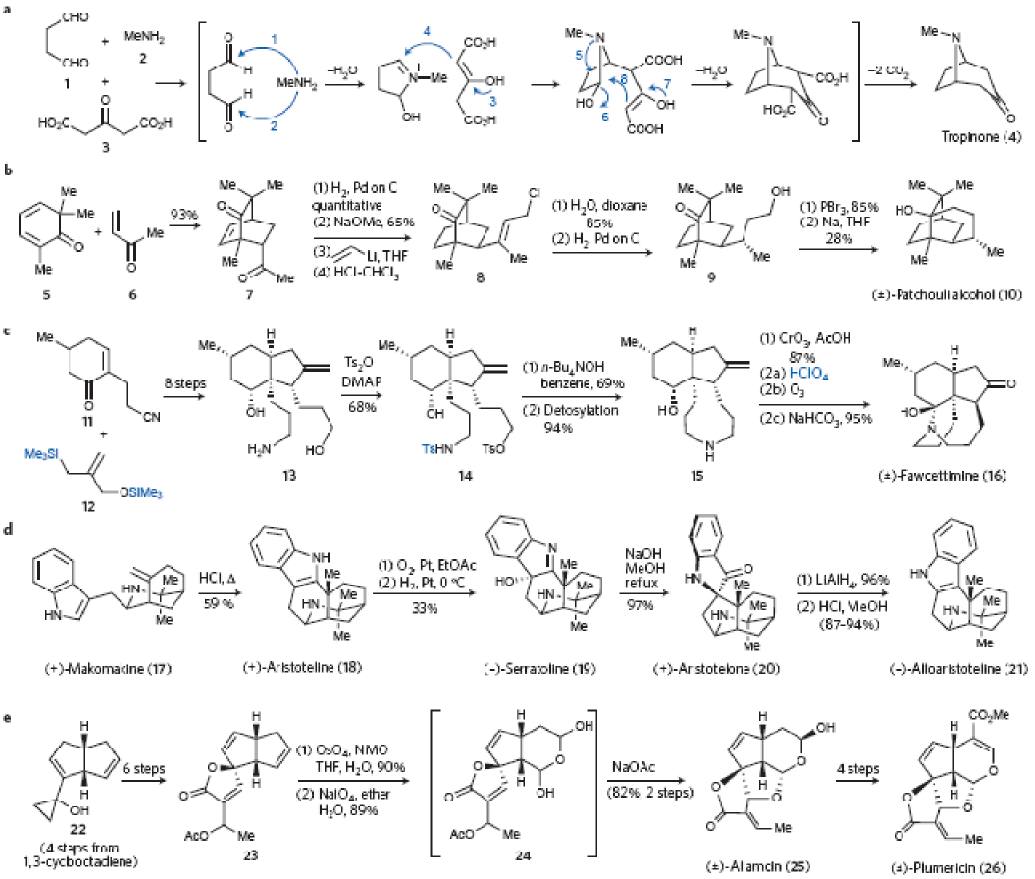
- Asymmetric Allylation of Methyl Ketones by Using Chiral Phenyl Carbinols
  Tietze, L. F.; Kinzel, T.; Wolfram, T. *Chem. Eur. J.* **2009**, *15*, 6199-6210.
  Abstract:



To methyl or to alkyl? High induced facial selectivities and excellent yields are obtained in the allylation of aliphatic methyl ketones by using a structurally simple phenylbenzyl auxiliary to give the corresponding homoallylic ethers (see scheme). The transferred auxiliary has a very good protecting quality and can easily be removed.

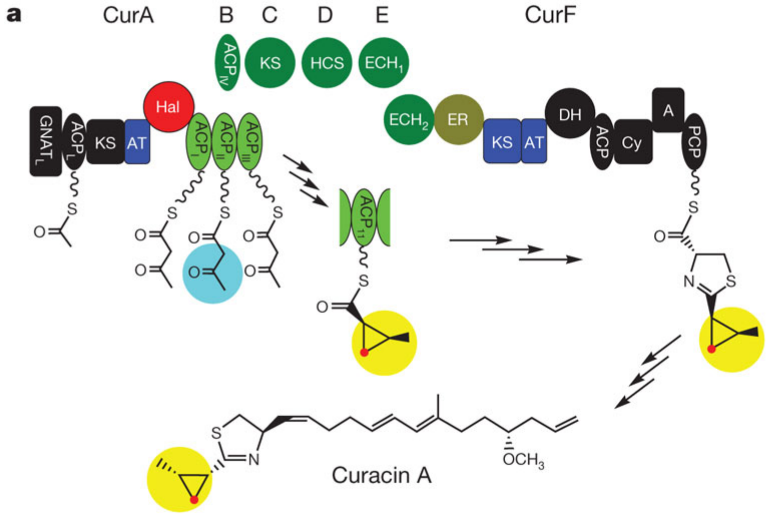
Novel chiral auxiliaries for the stereoselective allylation of aliphatic methyl ketones with allyltrimethylsilane and their use in the synthesis of homoallylic ethers are described. In a multicomponent domino process catalyzed by trifluoromethanesulfonic acid, the allyl moiety and the auxiliary are transferred onto the substrate to yield tertiary homoallylic ethers. The most useful auxiliary for a general application turned out to be the trimethylsilyl ether of phenyl benzyl carbinol with an induced diastereoselectivity of 90:10 using ethyl methyl ketone and 94:6 using isopropyl methyl ketone as substrates. The transferred substituted benzyl moiety has good protecting properties in subsequent transformations and can easily be removed under reductive conditions to provide the corresponding homoallylic alcohol. The origin of the high selectivity could be elucidated by identifying the relevant transition states using quantum-chemical calculations. An excellent agreement between calculated and experimentally observed selectivities was obtained assuming an oxocarbenium ion as intermediate.

- Protecting-group-free synthesis as an opportunity for invention
  Young, I. S.; Baran, P. S. *Nature Chem.* **2009**, *1*, 193-205.
  Abstract:



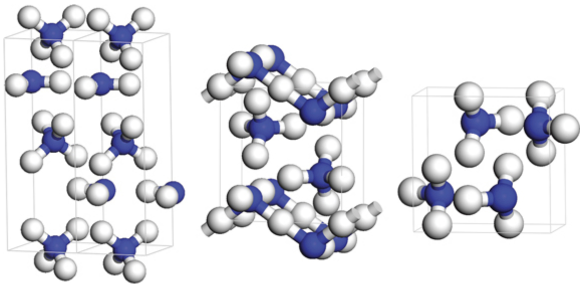
The constant pressure to prepare compounds in a more efficient manner has placed the process by which traditional synthetic*chemistry is conducted under scrutiny. Areas that have the potential to be improved must be highlighted and modified, so that we can approach the criterion of the ‘ideal synthesis'. One area that offers this prospect is the minimization of the use of protecting groups in synthesis. A protection/deprotection event introduces at least two steps into a sequence, incurring costs from additional reagents and waste disposal, and generally leads to a reduced overall yield. Here we present relevant historical context and highlight recent (post-2004) total syntheses that have developed new chemistry in an effort to exclude protecting groups. The invention of chemoselective methodologies is crucial to the execution of 'protecting-group-free' synthesis, and recent advances in this area are also highlighted.

- Metamorphic enzyme assembly in polyketide diversification
  Gu, L.; Wang, B.; Kulkarni, A.; Geders, T. W.; Grindberg, R. V.; Gerwick, L.; Håkansson, K.; Wipf, P.; Smith, J. L.; Gerwick, W. H.; Sherman, D. H. *Nature* **2009**, *459*, 731- 735.
  <u>Abstract:</u>



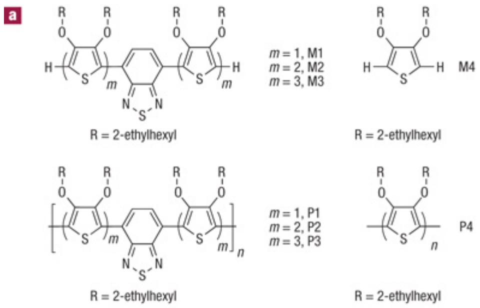
Natural product chemical diversity is fuelled by the emergence and ongoing evolution of biosynthetic pathways in secondary metabolism. However, co-evolution of enzymes for metabolic diversification is not well understood, especially at the biochemical level. Here, two parallel assemblies with an extraordinarily high sequence identity from *Lyngbya majuscula* form a β-branched cyclopropane in the curacin A pathway (Cur), and a vinyl chloride group in the jamaicamide pathway (Jam). The components include a halogenase, a 3-hydroxy-3-methylglutaryl enzyme cassette for polyketide β-branching, and an enoyl reductase domain. The halogenase from CurA, and the dehydratases (ECH_1s), decarboxylases (ECH_2s) and enoyl reductase domains from both Cur and Jam, were assessed biochemically to determine the mechanisms of cyclopropane and vinyl chloride formation. Unexpectedly, the polyketide β-branching pathway was modified by introduction of a γ-chlorination step on (*S*)-3-hydroxy-3-methylglutaryl mediated by Cur halogenase, a non-haem Fe(II), α-ketoglutarate-dependent enzyme. In a divergent scheme, Cur ECH_2 was found to catalyse formation of the α,β enoyl thioester, whereas Jam ECH_2 formed a vinyl chloride moiety by selectively generating the corresponding β,γ enoyl thioester of the 3-methyl-4-chloroglutaconyl decarboxylation product. Finally, the enoyl reductase domain of CurF specifically catalysed an unprecedented cyclopropanation on the chlorinated product of Cur ECH_2 instead of the canonical α, β C = C saturation reaction. Thus, the combination of chlorination and polyketide β-branching, coupled with mechanistic diversification of ECH_2 and enoyl reductase, leads to the formation of cyclopropane and vinyl chloride moieties. These results reveal a parallel interplay of evolutionary events in multienzyme systems leading to functional group diversity in secondary metabolites.

- Highly compressed ammonia forms an ionic crystal
  Pickard, C. J.; Needs, R. J. *Nature Materials* **2008**, *7*, 775-779.
  Abstract:



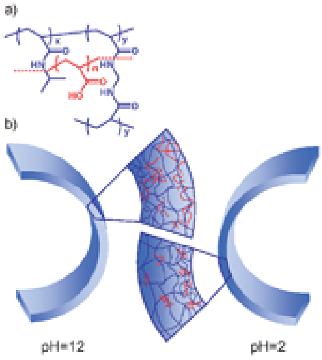
Ammonia is an important compound with many uses, such as in the manufacture of fertilizers, explosives and pharmaceuticals. As an archetypal hydrogen-bonded system, the properties of ammonia under pressure are of fundamental interest, and compressed ammonia has a significant role in planetary physics. We predict new high-pressure crystalline phases of ammonia (NH3) through a computational search based on first-principles density-functional-theory calculations. Ammonia is known to form hydrogen-bonded solids, but we predict that at higher pressures it will form ammonium amide ionic solids consisting of alternate layers of NH4+ and NH2- ions. These ionic phases are predicted to be stable over a wide range of pressures readily obtainable in laboratory experiments. The occurrence of ionic phases is rationalized in terms of the relative ease of forming ammonium and amide ions from ammonia molecules, and the volume reduction on doing so. We also predict that the ionic bonding cannot be sustained under extreme compression and that, at pressures beyond the reach of current static-loading experiments, ammonia will return to hydrogen-bonded structures consisting of neutral NH3 molecules.

- The donor–acceptor approach allows a black-to-transmissive switching polymeric electrochrome
  Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. *Nature Materials* **2008**, *7*, 795-799.
  Abstract:



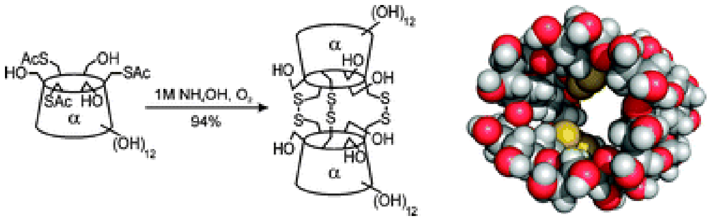
In the context of the fast-growing demand for innovative high-performance display technologies, the perspective of manufacturing low-cost functional materials that can be easily processed over large areas or finely printed into individual pixels, while being mechanically deformable, has motivated the development of novel electronically active organic components fulfilling the requirements for flexible displays and portable applications. Among all technologies relying on a low-power stimulated optical change, non-emissive organic electrochromic devices (ECDs) offer the advantage of being operational under a wide range of viewing angles and lighting conditions spanning direct sunlight as desired for various applications including signage, information tags and electronic paper. Combining mechanical flexibility, high contrast ratios and fast response times, along with colour tunability through structural control, polymeric electrochromes constitute the most attractive organic electronics for tomorrow's reflective/transmissive ECDs and displays. Although red, blue and most recently green electrochromic polymers (ECPs) required for additive primary colour space were investigated, attempts to make saturated black ECPs have not been reported, probably owing to the complexity of designing materials absorbing effectively over the whole visible spectrum. Here, we report on the use of the donor–acceptor approach to make the first neutral-state black polymeric electrochrome. Processable black-to-transmissive ECPs promise to affect the development of both reflective and transmissive ECDs by providing lower fabrication and processing costs through printing, spraying and coating methods, along with good scalability when compared with their traditional inorganic counterparts.

- Hydrogel logic gates using gradient semi-IPNs.
  Asoh, T. A.; Akashi, M. *Chem. Commun.* **2009**, 3548 – 3550.
  Abstract:



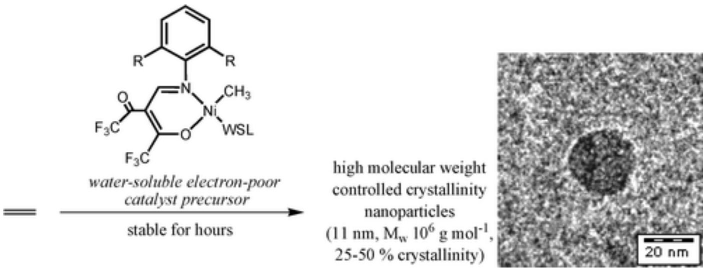
Gradient semi-IPNs consisting of thermoresponsive hydrogels and graded pH-responsive linear polymers were fabricated via electrophoresis and subsequent polymerization; gradient semi-IPNs bent in response to both pH and temperature.

- Tubular duplex -cyclodextrin triply bridged with disulfide bonds: synthesis, crystal structure and inclusion complexes.
  Krejí, L.; Budínský, M.; Císaová, I.; Kraus, T. *Chem. Commun.* **2009**, 3557 – 3559.
  Abstract:



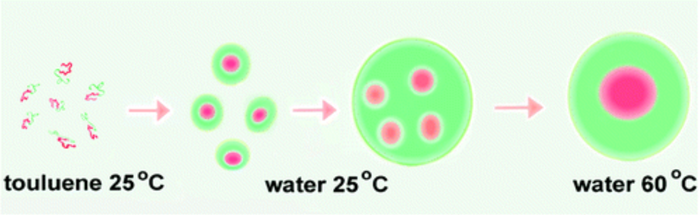
Template-free oxidative dimerization of 6^{I}, 6^{III}, 6^{V}-trisulfanyl--cyclodextrin proceeds with a remarkable efficiency (94%) yielding an unprecedented duplex -cyclodextrin triply bridged with disulfide linkages whose structure has been confirmed by X-ray analysis.

- Variable Crystallinity Polyethylene Nanoparticles
  Yu, S.-M.; Mecking, S. *Macromolecules* **2009**, *42*, 3669-3673.
  Abstract:



Water-soluble complexes based on enolatoimine ligands bearing electron-withdrawing trifluoromethyl groups [κ^2-*N*,*O*-{2,6-$R_2C_6H_3$*N*═C(H)C($COCF_3$)═C(*O*)CF_3}NiMe(L)] (**1a**, *R* = 3,5-$(CF_3)_2C_6H_3$, L = $Me(OCH_2CH_2)_nNH_2$; **1b**, *R* = 3,5-$(CF_3)_2C_6H_3$, L = TPPDS; **2b**, R = ^{i}Pr, L = TPPDS; **2c**, R = ^{i}Pr, L = TPPTS with TPPDS = PhP(*p*-$C_6H_4SO_3Na)_2$ and TPPTS = P(*m*-$C_6H_4SO_3Na)_3$) were prepared. These complexes polymerize ethylene to very small (10–30 nm) semicrystalline particles of high molecular weight (up to M_w 1.6 × 10^6 g mol^{-1}) polymer with a degree of branching (7–63 branches per 1000 C atoms) and thus crystallinity (≤25–50%) and melt transition temperatures (T_m = 75–129 °C) variable over a large range, depending on the substituents of the *N*-aryl moiety (2,6-$R_2C_6H_3$), and the polymerization temperature. The catalysts are stable for hours under polymerization conditions (50 °C) in the highly disperse aqueous system.

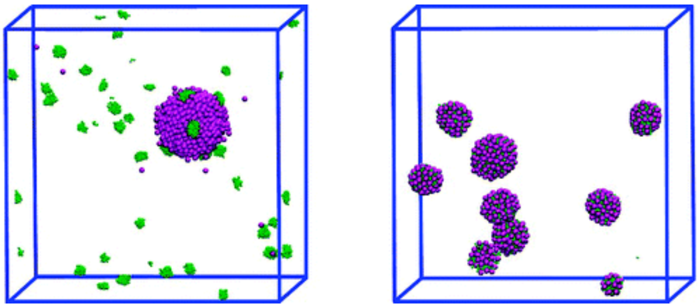
- Double-Crystalline Polyethylene-*b*-poly(ethylene oxide) with a Linear Polyethylene Block: Synthesis and Confined Crystallization in Self-Assembled Structure Formed from Aqueous Solution.
  Li, T.; Wang, W. J.; Liu, R.; Liang, W. H.; Zhao, G. F.; Li, Z. Y.; Wu, Q.; Zhu, F. M. *Macromolecules* **2009**, *42*, 3804–3810.
  Abstract:



Narrowly distributed polyethylene-*b*-poly(ethylene oxide) diblock copolymers (PE-*b*-PEO) with a linear PE block were successfully synthesized by combination of click coupling reaction of azido-terminated polyethylene (PE−N_3) and alkynyl-terminated poly(ethylene oxide) (PEO−$CONHCH_2C{\equiv}CH$). PE−N_3 derived from tosylation and subsequent substitution by sodium azide of hydroxyl-terminated PE (PE−OH) which was prepared by means of chain shuttling ethylene polymerization with 2,6-bis[1-(2,6- dimethylphenyl)imino ethyl] pyridine iron (II) dichloride (complex **1**)/methylaluminoxane (MAO)/diethyl zinc ($ZnEt_2$) and subsequent in situ oxidation with oxygen. PEO−$CONHCH_2C{\equiv}CH$ was synthesized through esterification the hydroxyl end-group on hydroxyl-terminated PEO (PEO−OH) with phosgene and subsequent amidation by propargyl amine. The self-assembly of three double-crystalline PE-*b*-PEO samples with different block length in water were investigated by laser light scattering (LLS) and transmission electron microscopy (TEM). It was found that, in water, a solvent selectively good for the PEO block, PE-*b*-PEO chains with proper PE block length could form spherical multicores micelles with the insoluble and crystallized PE blocks as the multicores and the soluble and swollen PEO blocks as the shell. These multicores in one micelle could reaggregate to a single-core as temperature increased. Differential scanning calorimetry (DSC) experiments showed that the

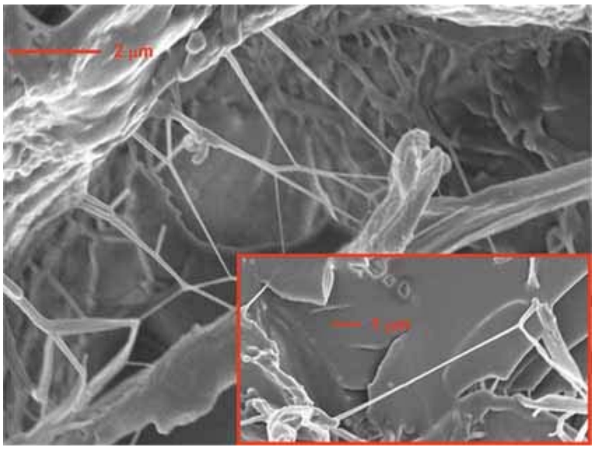
crystallization of both PE and PEO blocks was intensely confined by the previously self-assembled structure of PE-*b*-PEO in aqueous solution.

- Protected Peptide Nanoparticles: Experiments and Brownian Dynamics Simulations of the Energetics of Assembly
  Chen, T.; D'Addio, S. M.; Kennedy, M. T.; Swietlow, A.; Kevrekidis, I. G.; Panagiotopoulos, A. Z.; Prud'homme, R. K. *Nano Lett.* **2009**, *9*, 2218–2222.
  Abstract:



Soluble peptides, susceptible to degradation and clearance in therapeutic applications, have been formulated into protected nanoparticles for the first time through the process of kinetically controlled, block copolymer directed rapid precipitation using Flash NanoPrecipitation. Complementary Brownian dynamics simulations qualitatively model the nanoparticle formation process. The simulations corroborate the hypothesis that the size of nanoparticles decreases with increasing supersaturation. Additionally, the influence of the polymer-peptide interaction energy on the efficiency of nanoparticle protection by polymer surface coverage is elucidated in both experiments and simulations.

- Heterogeneity in Epoxy Nanocomposites Initiates Crazing: Significant Improvements in Fatigue Resistance and Toughening
  Zhang, W.; Srivastava, I.; Zhu, Y.-F.; Picu, C. R.; Koratkar, N. A. *Small* **2009**, *5*, 1403 – 1407.
  Abstract:



Amido-amine-functionalized multiwalled carbon-nanotube fillers fundamentally alter the fracture and fatigue behavior of a thermosetting epoxy by initiating crazing in the material (see image). The crazing results in over an order of magnitude reduction in fatigue crack growth rates and significant improvements in fracture toughness and ductility without any softening of the material.