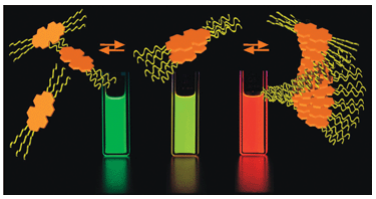
- Self-assembled π-stacks of functional dyes in solution: structural and thermodynamic features
  Chen, Z.; Lohr, A.; Saha-Möller, C. R.; Würthner, F. *Chem. Soc. Rev.* **2009**, *38*, 564 – 584.
  Abstract:

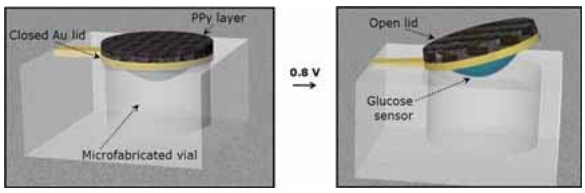


This *critical review* provides an overview on the formation of π-stacks of functional dyes in solution, aiming to acquaint young researchers with this topical research field and to stimulate further advance in supramolecular dye chemistry. Different mathematical models that have been proposed and applied for the description of aggregation equilibria of π-systems in solution are discussed. The factors that have significant impact on the structural features of aggregates and the thermodynamics of π–π stacking such as electrostatic interactions, size and geometry of the dye molecules are covered in this review. A comparison of the binding strength is made for different classes of functional π-conjugated systems, from simple benzene to more extended polycyclic hydrocarbon molecules, including triphenylenes and hexabenzocoronenes, heteroaromatic porphyrins and phthalocyanines, quadrupolar naphthalene and perylene bisimides, dipolar or even zwitterionic merocyanines and squaraines, and some macrocyclic dyes. Solvent effects on binding constants are analysed by linear free energy relationships with various solvent polarity scales (98 references with multiple entries).

- Amide bond formation: beyond the myth of coupling reagents
  Valeur, E.; Bradley, M. *Chem. Soc. Rev.* **2009**, *38*, 606 – 631.
  Abstract:

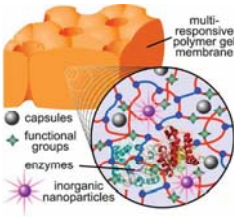
Amide bond formation is a fundamentally important reaction in organic synthesis, and is typically mediated by one of a myriad of so-called coupling reagents. This critical review is focussed on the most recently developed coupling reagents with particular attention paid to the pros and cons of the plethora of "acronym" based reagents. It aims to demystify the process allowing the chemist to make a sensible and educated choice when carrying out an amide coupling reaction (179 references).

- Integrating Biosensors and Drug Delivery: A Step Closer Toward Scalable Responsive Drug-Delivery Systems.
  Tsai, H.-K. A.; Moschou, E. A.; Daunert, S.; Madou, M.; Kulinsky, L. *Adv. Mater*. **2009**, 21, 656-660.
  Abstract:



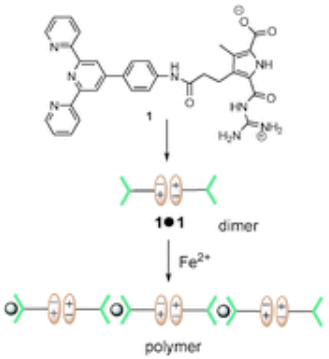
A miniature biosensor immobilized on the backside of a gold lid is protected inside a microfabricated vial. To activate the protected biosensor, the conjugated polymer/gold lid is opened by the application of 800 mV. Both independent sensing and drug delivery from the microvalves are demonstrated.

- Multiresponsive, Hierarchically Structured Membranes: New, Challenging, Biomimetic Materials for Biosensors, Controlled Release, Biochemical Gates, and Nanoreactors.
  Tokarev, I.; Minko, S. *Adv. Mater*. **2009**, 21, 241-247.
  Abstract:



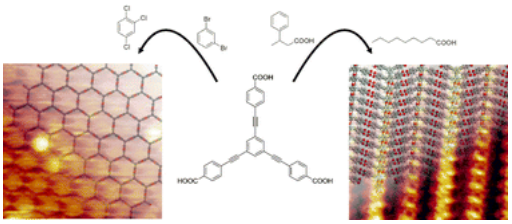
Multifunctional responsive gel membranes present a new and promising platform for the development of smart devices for bioseparation, biosensors, and smart drug release. These membranes combine the functions of stimuli-responsive control and regulation of the mass transport with a range of properties, such as storage, catalysis of chemical reactions, antimicrobial activity, and optical signal transduction.

- Step-wise self-assembly of a small molecule with two orthogonal binding interactions leads to single stranded linear polymers in DMSO.
  Gröger, G.; Stepanenko, V.; Würthner, F.; Schmuck, C. *Chem. Commun.* **2009**, 698 – 700.
  Abstract:



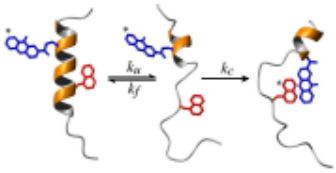
The step-wise self-assembly of a small, self-complementary monomer with two orthogonal binding interactions, ion pairing and metal–ligand binding, is described; zwitterion **1** forms ion paired dimers in DMSO which, upon addition of 0.5 equivalents of Fe(II), aggregate into single stranded linear polymers.

- Aromatic interaction *vs.* hydrogen bonding in self-assembly at the liquid–solid interface.
  Gutzler, R.; Lappe, S.; Mahata, K.; Schmittel, M.; Heckl, W. M.; Lackinger, M. *Chem. Commun.* **2009**, 680 – 682.
  Abstract:



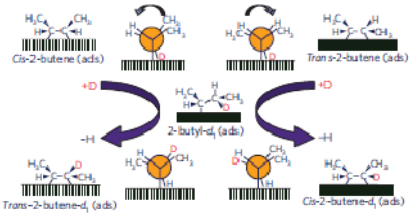
Interfacial self-assembly of specific monolayer structures from solution on a graphite surface can be steered by tuning the interplay between solute–solute and solute–solvent interactions.

- Local conformational dynamics in α-helices measured by fast triplet transfer
  Fierza, B.; Reinerb, A.; Kiefhaberb, T. *Proc. Nat. Acad. Sci.* **2009**, *106*, 1057–1062**.**
  Abstract**:**



Coupling fast triplet–triplet energy transfer (TTET) between xanthone and naphthylalanine to the helix–coil equilibrium in alanine-based peptides allowed the observation of local equilibrium fluctuations in α-helices on the nanoseconds to microseconds time scale. The experiments revealed faster helix unfolding in the terminal regions compared with the central parts of the helix with time constants varying from 250 ns to 1.4 µs at 5 °C. Local helix formation occurs with a time constant of ≈400 ns, independent of the position in the helix. Comparing the experimental data with simulations using a kinetic Ising model showed that the experimentally observed dynamics can be explained by a 1-dimensional boundary diffusion with position-independent elementary time constants of ≈50 ns for the addition and of ≈65 ns for the removal of an α-helical segment. The elementary time constant for helix growth agrees well with previously measured time constants for formation of short loops in unfolded polypeptide chains, suggesting that helix elongation is mainly limited by a conformational search.

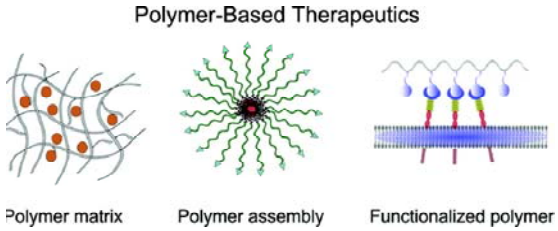
- Tuning selectivity in catalysis by controlling particle shape
  Lee, I.; Delbec, F.; Morales, R.; Albiter, M. A.; Zaera, F. *Nat. Mater.* **2009**, *8*, 132 -138.
  Abstract:



A catalytic process for the selective formation of *cis* olefins would help minimize the production of unhealthy *trans* fats during the partial hydrogenation of edible oils. Here we report on the design of such a process on the basis of studies with model systems. Temperature programmed desorption data on single crystals showed that the isomerization of *trans* olefins to their *cis* counterparts is promoted by (111) facets of platinum, and that such selectivity is reversed on more open surfaces. Quantum mechanics calculations suggested that the extra stability of *cis* olefins seen on hydrogen-saturated Pt(111) surfaces may be due to a lesser degree of surface reconstruction, a factor found to

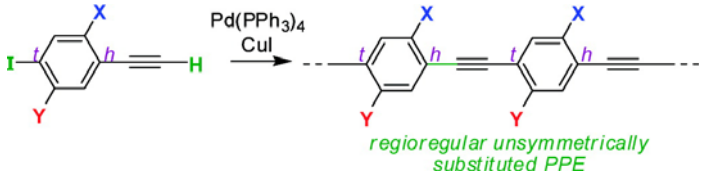
be significant in the adsorption on close-packed platinum surfaces. Kinetic data using catalysts made out of dispersed tetrahedral Pt nanoparticles corroborated the selective promotion of the *trans*-to-*cis* isomerization on the (111) facets of the metal. Our work provides an example for how catalytic selectivity may be controlled by controlling the shape of the catalytic particles.

- Polymer-Based Therapeutics
  Liu, S.; Maheshwari, R.; Kiick, K. L. *Macromolecules* **2009**, *42*, 3-13.
  Abstract :



Polymeric materials have been applied in therapeutic applications, such as drug delivery and tissue regeneration, for decades owing to their biocompatibility and suitable mechanical properties. In addition, select polymer-drug conjugates have been used as bioactive pharmaceuticals owing to their increased drug efficacy, solubility, and target specificity compared with small-molecule drugs. Increased synthetic control of polymer properties has permitted the production of polymer assemblies for the targeted and controlled delivery of drugs, and polymeric sequestrants take advantage of their lack of solubility for the sequestration of target molecules in vivo. In more recent studies reviewed in greater detail here, the properties of polymers that distinguish them from small-molecule drugs, such as their high molecular weight and their ability to display multiple pendant moieties, have been specifically exploited for activating cellular targets or inhibiting the binding of pathogens. The elucidation of relevant structure-function relationships in investigations of this kind has relied on the combination of living polymerization methods with chemical conjugation methods, and protein engineering methods have shown increasing potential in the manipulation of architectural features of such polymer therapeutics. Garnering a detailed understanding of the various mechanisms by which multivalent polymers engage biological targets is certain to expand the role of polymers as therapeutics, by enabling highly specific activities of designed polymers in the biological environment.

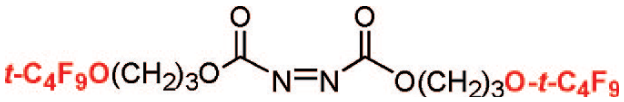
- Synthetic Approaches to Regioregular Unsymmetrical Dialkoxy-Substituted Poly(1,4-phenylene ethynylene)s
  Nambiar, R.; Woody, K. B.; Ochocki, J. D.; Brizius, G. L.; Collard, D. M. *Macromolecules* **2009**, *42*, 43-51.
  Abstract :



Poly(2,5-disubstituted-1,4-phenylene ethynylene)s, PPEs, are generally synthesized by Pd-catalyzed coupling polymerizations of appropriately substituted 1,4-diiodobenzenes and 1,4-diethynylbenzenes (i.e., condensation polymerization of A-A and B-B type monomers). If the monomers are not symmetrically substituted, this results in an irregular substitution pattern of the side chains along the

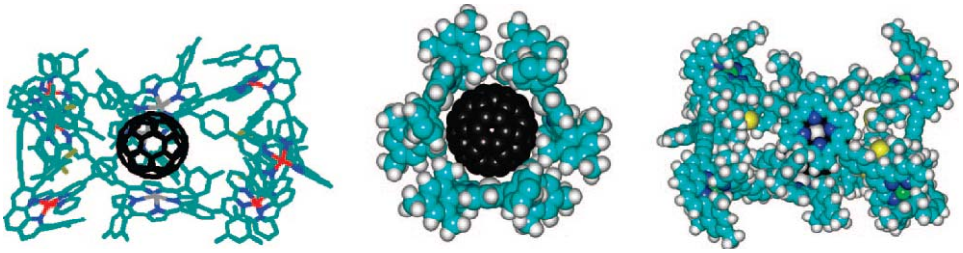
polymer backbone. As with other classes of conjugated polymers, the relative placement of side chains along the backbone should influence the properties of the materials. We report a new synthetic approach to prepare regioregular unsymmetrically substituted PPEs by polymerization of 4-iodophenylacetylenes (i.e., a condensation polymerization of a single A-B type monomer). We have synthesized both the regiorandom and regioregular PPEs from unsymmetrically substituted monomers. We provide a detailed discussion of various approaches to the synthesis of PPEs with different regioregularities and provide a preliminary description of the differences between regioregular and regiorandom analogues.

- Second-Generation Tags for Fluorous Chemistry Exemplified with a New Fluorous Mitsunobu Reagent
  Chu, Q.; Henry, C.; Curran, D. P. *Org. Lett*. **2008**, *10*, 2453-2456.
  Abstract :



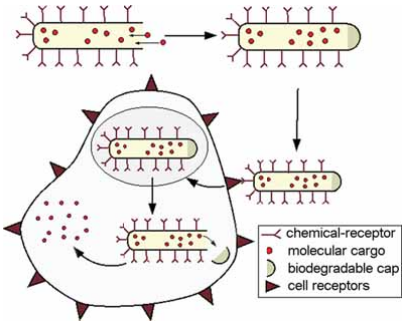
A new fluorous DEAD reagent bearing two perfluoro-*tert*-butyloxy groups with propylene spacers shows excellent promise for use in fluorous Mitsunobu reactions. Pure target products were obtained in good yields after removing fluorous byproducts by FSPE. The new reagent serves as a prototype for a greener second generation of fluorous reagents bearing tags that are not expected to degrade in the environment to compounds that are highly persistent or that bioaccumulate in higher organisms.

- Supramolecular Multicomponent Self-Assembly of Shape-Adaptive Nanoprisms: Wrapping up C_{60} with Three Porphyrin Units
  Schmittel, M.; He, B.; Mal, P. *Org. Lett*. **2008**, *10*, 2513-2516.
  Abstract :



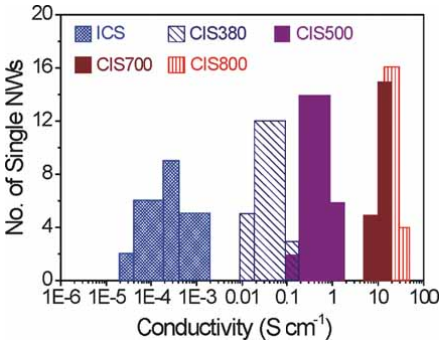
Self-assembly of a C_{3v} symmetric trisphenanthroline and linear bisterpyridines in the presence of Cu^{+} did not furnish the expected supramolecular nanoprisms in quantitative yield. With an accurately sized tripyridine as a stabilizing template, the nanoprism formed exclusively. Furthermore, an adaptive constriction of the nanoprism was seen with C_{60} as template: as a result of the smaller size of C_{60} the nanoframework wrapped up around the guest like an accordion-type host system.

- Modeling the Loading and Unloading of Drugs into Nanotubes
  Hilder, T. A.; Hill, J. M. *Small* **2009**, *5*, 300-308.
  Abstract:



One of the most promising applications of nanotechnology is that of drug delivery, and in particular the targeted delivery of drugs using nanotubes. Functionalized nanotubes might be able to target specific cells, become ingested, and then release their contents in response to a chemical trigger. This will have significant implications for the future treatment of patients, particularly those suffering from cancer, for whom presently the nonspecific nature of chemotherapy often kills healthy normal cells. Research to date has largely been through experiments investigating toxicity, biocompatibility, solubility, functionalization, and cellular uptake. More recently, the loading and unloading of molecular cargo has gained momentum from both experimental and theoretical investigations. This Review focuses on the loading and unloading of molecular cargo and highlights recent theoretical investigations, which to date have received very little attention in the review literature. The development of nanotube drug-delivery capsules is of vital concern for the improvement of medical treatment, and mathematical modeling tends to facilitate such development and provides a quicker route to applications of the technology. This Review highlights the latest progress in terms of theoretical investigations and provides a focus for the development of the next generation of medical therapeutics.

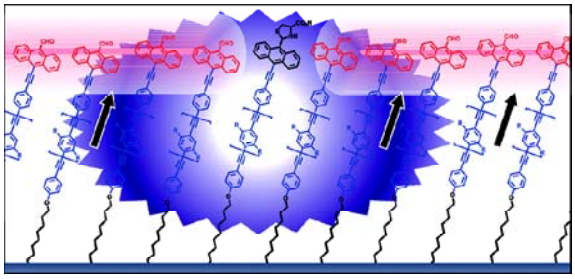
- Tuning Electrical and Photoelectrical Properties of CdSe Nanowires via Indium Doping
  He, Z.; Jie, J.; Zhang, W.; Zhang, W.; Luo, L.; Fan, X.; Yuan, G.; Bello, I.; Lee, S.-T. *Small* **2009**, *5*, 345-350.
  Abstract:



n-Type doping of CdSe nanowires is achieved by either co-evaporating indium at different temperatures during growth, or post-growth doping via a thermal diffusion process. The conductivity of CdSe nanowires is tuned reproducibly by nearly five orders of magnitude in a controlled way, and carrier concentration as high as $\sim 10^{19}$ cm^{-3} is reached (see image). The doped CdSe nanowires show high sensitivity to light irradiation.

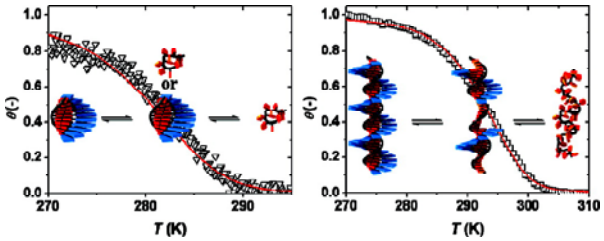
- Chemically Controlled Amplified Ratiometric Fluorescence in Surface-Immobilized End-Capped Oligo(p-phenylene ethynylene)s
  Acharya, J. R.; Zhang, H.; Li, X.; Nesterov, E. E. *J. Am. Chem. Soc.*, **2009**, *131*, 880–881.

Abstract:



Efficient photoexcitation energy transfer in extended π-electron conjugated molecules is a key factor in applications of such systems as a gain media in signal-amplifying fluorescent chemodetectors. Here we report an unprecedented ratiometric fluorescence amplification phenomenon in the surface-immobilized monolayers of oligo(p-phenylene ethynylene)s end-capped with a lower energy gap receptor group. The process of covalent immobilization on the surface results in monolayer films with improved molecular organization, which display highly efficient excitation energy transfer to the lower energy receptor groups. Chemical transformation of a subtle fraction of the receptor groups on the surface leads to a very significant fluorescent ratiometric response. While fundamental understanding of this unusual "turn-on" amplification phenomenon requires further studies, it can be used to develop thin-film ratiometric fluorescent chemosensors with improved optical gain.

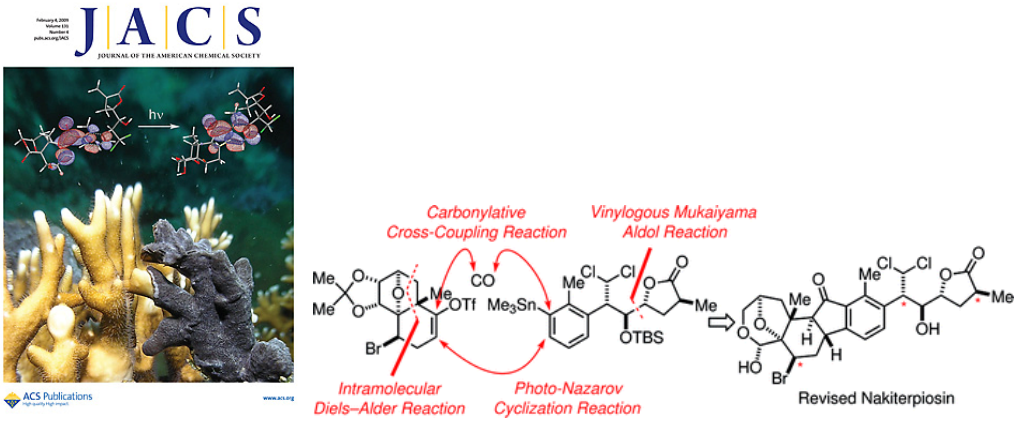
- Insights into Templated Supramolecular Polymerization: Binding of Naphthalene Derivatives to ssDNA Templates of Different Lengths
  Janssen, P. G. A.; Farouji, S.; Surin, M.; Vila, X.; Gielen, J. C.; de Greef, T. F. A.; Vos, M. R. J. ; Bomans, P. H. H.; Sommerdijk, N. A. J. M.; Christianen, P. C. M.; Leclere, P.; Lazzaroni, R.; Schoot, P.; Meijer, E. W.; Schennin, A. P. H. J. *J. Am. Chem. Soc.*, **2009**, *131*, 1222–1231.
  Abstract:



We report on two diaminotriazine-equipped naphthalene derivatives that bind reversibly to a single-stranded DNA template or "tape-measure molecule" via hydrogen bonding, yielding monodisperse double-stranded DNA hybrids with one strand consisting of a supramolecular naphthalene backbone. These assemblies have been investigated extensively, both experimentally and theoretically. The structure and the templated self-assembly process of the complex have been characterized with UV-vis spectroscopy, circular dichroism spectroscopy, molecular dynamics simulations, cryo-transmission electron microscopy, liquid atomic force microscopy, electrospray ionization mass spectrometry, light scattering, and 1H NMR and infrared spectroscopy. We have found that the DNA hybrid complexes have a right-handed helical arrangement stabilized by π-π interactions and hydrogen bonds. The hydrophilic hydroxyl group at the end of the ethylene glycol of the guest molecule suppressed both the nontemplated self-assembly of the naphthalene guest molecules and the further aggregation of the entire DNA hybrid complex. Through the use of a theoretical mass-action model for the templated self-assembly, the host-guest and guest-guest interaction energies were estimated by fitting to the spectroscopic data. The differently estimated values of the interaction energies and thermodynamic parameters vary within experimental error, showing the selfconsistency of the

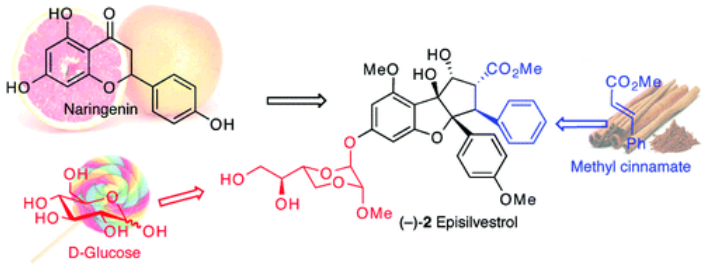
model. From the obtained correlation between the positions of the guest molecules bound on the template, we have obtained a qualitative theoretical picture of the way in which the guests are physically distributed on the templates. For short templates, the templates are filled one-by-one, even at moderate fractions of bound sites. For larger templates, the templates first have alternating sequences of filled and empty sections, after which, at large fractions of bound sites, virtually all of the binding sites for all template lengths are filled.

- Synthesis and Structure Revision of Nakiterpiosin
  Gao, S.; Wang, Q.; Chen, C. *J. Am. Chem. Soc.* **2009**, *131*, 1410–1412.
  Abstract:



This manuscript describes a convergent synthesis and the revision of the relative stereochemistry of nakiterpiosin, a marine C-nor-D-homosteroid. Our synthesis features a late-stage carbonylative Stille cross-coupling reaction and a photo-Nazarov cyclization reaction that deliver the complete nakiterpiosin skeleton efficiently. Light is key to the successful synthesis of nakiterpiosin, a novel C-nor-D-homosteroid isolated from cyanobacteriosponge *T. hoshinota*. Our synthesis work helps elucidate the correct relative configuration of this marine natural product.

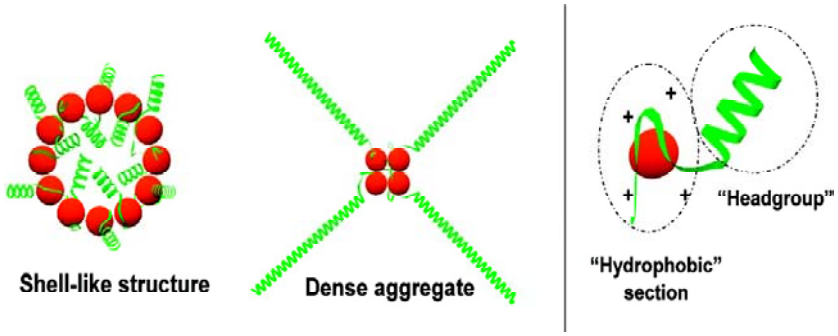
- Total Synthesis of the Potent Anticancer Aglaia Metabolites (−)-Silvestrol and (−)-Episilvestrol and the Active Analogue (−)-4'-Desmethoxyepisilvestrol
  Adams, T. E.; El Sous, M.; Hawkins, B. C.; Hirner, S.; Holloway, G.; Khoo, M. L.; Owen, D. J.; Savage, G. P.; Scammells, P. J.; Rizzacasa, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 1607–1616.
  Abstract:



Total synthesis of the anticancer 1,4-dioxane containing natural products silvestrol (**1**) and episilvestrol (**2**) is described by an approach based on the proposed biosynthesis of these novel compounds. The key steps included an oxidative rearrangement of the protected d-glucose derivative **11** to afford the 1,4-dioxane **12**, which could be elaborated to the coupling partner **5** and a photochemical [3 + 2]-cycloadditon between the 3-hydroxyflavone **27** and methyl cinnamate followed by base-induced α-ketol rearrangement and reduction to give the cyclopentabenzofuran

core **33**. The core (−)-**6** and 1,4-dioxane fragment **5** were united by a highly stereoselective Mitsunobu coupling with the modified azodicarboxylate DMEAD to afford the axial coupled product **36**. Deprotection then gave episilvestrol (**2**). Silvestrol (**1**) was synthesized by a coupling between core (−)-**6** and the dioxane **44** followed by deprotection. Compound **1** was also synthesized from episilvestrol (**2**) by a Mitsunobu inversion. In addition, the analogue 4'-desmethoxyepisilvestrol (**46**) was synthesized via the same route. It was found that **46** and episilvestrol **2** displayed an unexpected concentration-dependent chemical shift variation for the nonexchangeable dioxane protons. Synthetic compounds **1**, **2**, **38**, **46**, and **54** were tested against cancer cells lines, and it was found that the stereochemistry of the core was critical for activity. Synthetic analogue 4'-desmethoxyepisilvestrol (**46**) was also active against lung and colon cancer cell lines.

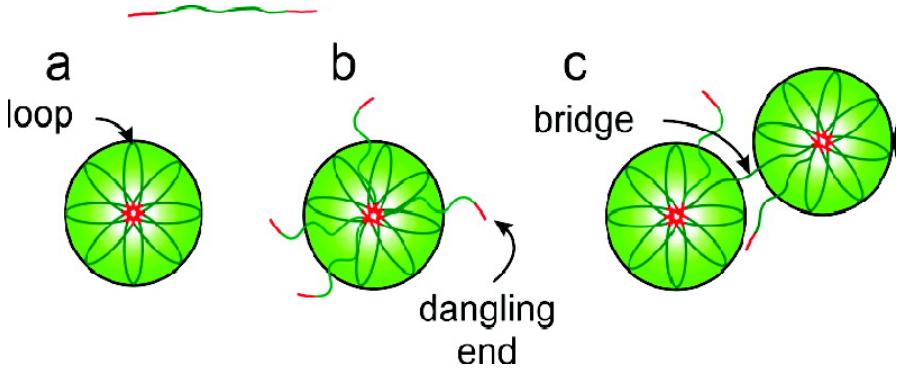
- Supramolecular Assembly of Block Copolypeptides with Semiconductor Nanocrystals
  Atmaja, B.; Cha, J. N.; Marshall, A.; Frank, C. W. *Langmuir* **2009**, *25*, 707-715.
  Abstract:



We report the analogy between the self-assembly properties of amphiphilic phospholipids and the similar behavior observed for quantum dot (CdSe/CdS)-diblock copolypeptide hybrid systems, and the effect of the self-assembly on secondary structures of the polypeptides. At neutral pH, the diblock copolypeptide, oly(diethyleneglycol-Llysine)- poly(L-lysine), comprises a positively charged poly-L-lysine (PLL) block and a hydrophilic and uncharged poly(diethyleneglycol-L-lysine) (PEGLL) block. By itself, the copolypeptide is *not* amphiphilic. However, when the polymers are mixed with water-soluble, negatively charged, citrate-functionalized quantum dots (QDs) in water, shell-like structures or dense aggregates are spontaneously formed. Electrostatic and hydrogen-bonding interactions between the positively charged PLL residues and the negatively charged ligands on the QDs lead to charge neutralization of the PLL block, while the PEGLL block remains hydrophilic. As a result, a pseudo "amphiphilic" molecular unit is formed in which the "hydrophobic" and hydrophilic sections constitute the charge-neutralized PLL residues together with the associating QD and the remaining polypeptide residues that are not neutralized, respectively. The generation of these "amphiphilic" molecular units in turn drives the formation of the QD-polypeptide assemblies. Support for this analogy comes from the observed transition in the shape of the assembly from a shell-like structure to a dense aggregate that is very much analogous to the vesicle-to-micelle transition observed in lipid systems. Furthermore, this shape transition can be explained qualitatively using a concept that is analogous to the surfactant number (*N*) *a*hc/*a*hg), which has been applied extensively in amphiphilic lipid systems. Specifically, as the ratio of the "hydrophobic" area (*a*hc) to the hydrophilic area (*a*hg) decreases, a shape transition from the shell-like structure to the dense aggregate occurs. In addition, the size of the shell-like structure changes as a function of the dimensions of the "amphiphilic molecular unit in a manner that is similar to how the size of the lipid vesicle changes with the dimensions of the lipid molecule. Circular dichroism (CD) measurements

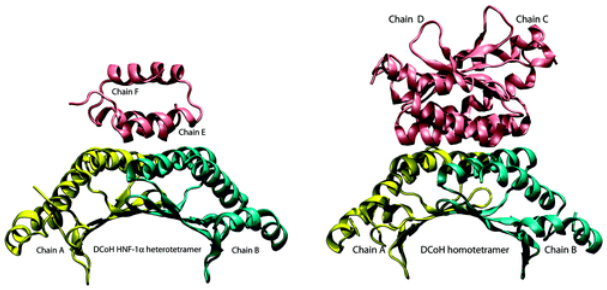
have shown that the PEGLL-PLL molecule has a well-defined secondary structure (R-helical PEGLL block and random coil PLL block) that remains virtually unchanged after reacting with the QDs. This finding is consistent with the hypothesis that it is the electrostatic interaction between the amines on the PLL block and the citrate ligands on the QDs that drives the self-assembly.

- Aggregation Behavior of a New Series of ABA Triblock Copolymers Bearing Short Outer A Blocks in B-Selective Solvent: From Free Chains to Bridged Micelles
  Giacomelli, F. C.; Riegel, I. C.; Petzhold, C. L.; da Silveira, N. P.; Stepanek, P. *Langmuir* **2009**, *25*, 731-738.
  Abstract:



A combination of dynamic (DLS) and static (SLS) light scattering measurements was employed to study the self-assembly behavior of a new series of triblock copolymers bearing poly[5-(*N,N*-diethylamino isoprene)] (PAI) short outer blocks and polystyrene (PS) as the major middle block. Previously, it was verified that PAI outer blocks can be quaternized leading the formation of crew-cut aggregates in water (Riegel, I. C.; Eisenberg, A.; Petzhold, C. L.; Samios, D. *Langmuir* **2002**, *18,* 3358). Herein, we focus on the copolymer's ability in the nonquaternized version to undergo self-aggregation in dimethylformamide (DMF), a selective solvent for the middle block. Light scattering measurements showed that formation of well-defined flowerlike micelles is likely to occur. Aggregates with a relatively narrow distribution, small average size, and number of aggregation ranging from 21 to 39 chains/micelle were experimentally observed. The results also suggested that ~5-6 polymeric units per each short outer block are needed to induce aggregation. The middle block length governs the size of the micelles and influences the number of aggregation of the resultant particles as well. Furthermore, when the polystyrene middle block was particularly long (degree of polymerization DP > 600), dynamic and static light scattering measurements suggested the formation of bridged micelles in an open structure in concentrations as low as 15 mg mL^{-1}.

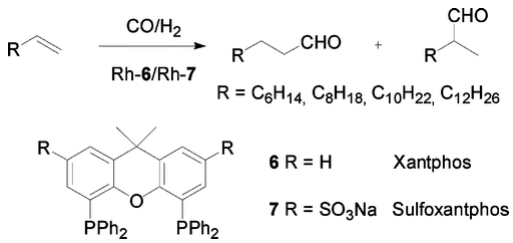
- Principles of Protein−Protein Interactions: What are the Preferred Ways For Proteins To Interact?
  Keskin, O.; Gursoy, A.; Ma, B.; Nussinov, R. *Chem. Rev.* **2008**, *108*, 1225-1244.
  Abstract:



Proteins are the working horse of the cellular machinery. They are responsible for diverse functions ranging from molecular motors to signaling. They catalyze reactions, transport, form the building blocks of viral capsids, traverse the membranes to yield regulated channels, and transmit the information from the DNA to the RNA. They synthesize new molecules, and they are responsible for their degradation. Proteins are the vehicles of the immune response and of viral entry into cells. The broad recognition of their involvement in all cellular processes has led to focused efforts to predict their functions from sequences, and if available, from their structures. A practical way to predict protein function is through identification of the binding partners. Since the vast majority of protein chores in living cells are mediated by protein−protein interactions, if the function of at least one of the components with which the protein interacts is identified, it is expected to facilitate its functional and pathway assignment. Through the network of protein−protein interactions, we can map cellular pathways and their intricate cross-connectivity. Since two protein partners cannot simultaneously bind at the same (or overlapping) site, discovery of the ways in which proteins associate should assist in inferring their dynamic regulation. Identification of protein−protein interactions is at the heart of functional genomics. Prediction of protein−protein interactions is also crucial for drug discovery. Knowledge of the pathway and its topology, length, and dynamics should provide useful information for forecasting side effects.

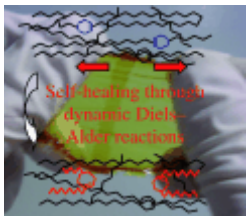
While it is important to predict protein associations, it is a daunting task. Some associations are obligatory, whereas others are transient, continuously forming and dissociating. From the physical chemical standpoint, any two proteins can interact. The question is under what conditions and at which strength. Protein−protein interactions are largely driven by the hydrophobic effect. Hydrogen bonds and electrostatic interactions play crucial roles, and covalent bonds are also important. Below, we aim to provide an overview of the principles of protein−protein interactions. Within this framework, we highlight what we consider are key components in the question of “what are the preferred ways for proteins to interact”. The goal is to be able to predict how the proteins will interact. Our assumption is that the structures are available and that there are experimental data that the proteins do interact. In the absence of such data, docking the structures of any pair of proteins will always find a matching patch of surface that may appear favorable.

- Hydroformylation in Room Temperature Ionic Liquids (RTILs): Catalyst and Process Developments
  Haumann, M.; Riisager, A. *Chem. Rev.* **2008**, *108*, 1474-1497.
  <u>Abstract:</u>



Over the last few years, ionic liquids have successfully been applied as alternative solvents for homogeneous biphasic catalysis. Many transition metal complexes dissolve readily in ionic liquids, which enables their use as solvents for transition metal catalysis. Sufficient solubility for a wide range of catalyst complexes is an obvious, but not trivial, prerequisite for a versatile solvent for homogeneous catalysis. Obviously, there are many other good reasons to apply ionic liquids as alternative solvents in transition metal-catalyzed reactions. Besides their very low vapor pressure and their good thermal stability, an important advantage is the possibility to tune their solubility and acidity/coordination properties by varying the nature of the anions and cations systematically.
In this review we will focus on the development of room temperature ionic liquids as alternative solvents for biphasic catalysis, exemplified for the hydroformylation reaction. The development of novel ionic liquids as well as ligands to match the requirements of biphasic catalysis will be discussed. Mechanistic studies including in situ IR and NMR techniques will be presented to signify similarities and differences when using ionic liquids as solvents instead of molecular organic solvents, and the novel concept of supported ionic liquid-phase (SILP) catalysis and catalytic systems comprising $scCO_2$ are included to enlighten the potential of ionic liquids as optional reaction media for process designs applying continuous fixed-bed reactions.

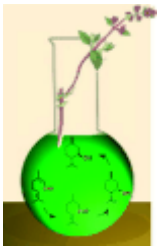
- Room Temperature Dynamic Polymers Based on Diels-Alder Chemistry
  P. Reutenauer, E. Buhler, P. J. Boul, S. J. Candau, J.-M. Lehn *Chem. Eur. J.* **2009**,*15*, 1893-1900.
  Abstract:



Polymer, heal thyself! Dynamic polymers formed by a reversible Diels-Alder reaction were formed and studied by using neutron scattering at room temperature. They were used to obtain thin films that displayed self-healing at room temperature (see figure). Dynamers based on reversible Diels-Alder chemistry have been obtained and shown to undergo dynamic exchange at room temperature. Their study in solution by small-angle neutron scattering indicated the formation of long and highly flexible chains. Polydispersed molecules gave T_g values below room temperature, permitting the generation of a dynamic elastomer upon introduction of a dynamic cross-linking agent. The use of a system with a low equilibrium constant gives access to materials with interesting self-healing properties.

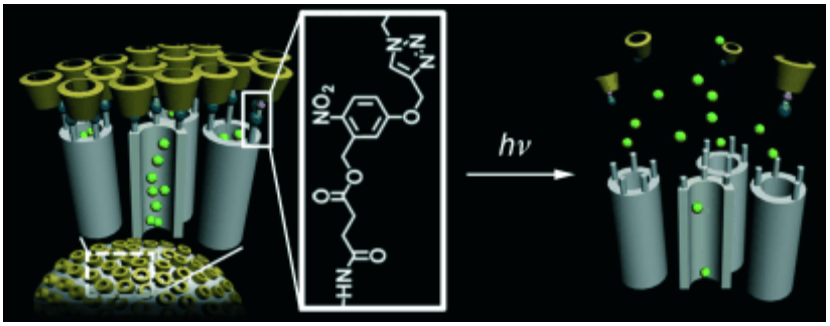
- Zr-Zeolite Beta: A New Heterogeneous Catalyst System for the Highly Selective Cascade Transformation of Citral to (±)-Menthol
  Nie, Y.; Jaenicke, S.; Chuah, G.-K. *Chem. Eur. J.* **2009**,*15*, 1991-1999.

Abstract:



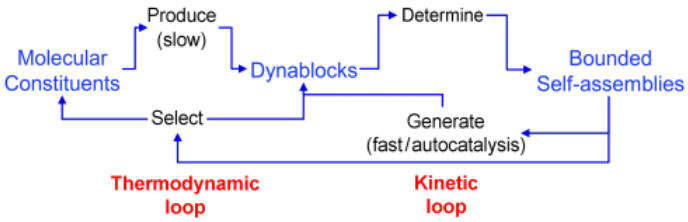
Minty green: Zr-zeolite beta (Zr-beta) directs the one-pot catalytic cascade transformation of citral to menthols with high diastereoselectivity. The solid catalyst, a bifunctional Ni/Zr-beta or a composite Zr-beta-Ni/MCM-41 system, is easily recovered and reused in this green synthetic method (see figure). The transformation of citral to menthols involves hydrogenation steps as well as cyclisation of the intermediate, citronellal. The ability of Zr-zeolite beta to catalyse the cyclisation with high diastereoselectivity to (±)-isopulegol is the critical step in this cascade transformation. Bifunctional catalysts containing nickel or rhodium supported on Zr-zeolite beta gave menthols in yields of 87-89 % and an excellent diastereoselectivity of 94 % for the desired (±)-menthol. Dual catalyst systems of Zr-zeolite beta and nano-dispersed Ni on an MCM-41 support were equally effective and have the added advantage that the rates of the acid- and hydrogenation-catalysed steps can be independently varied. By applying a pressure ramp of 0.2-2 MPa, the yield of menthols could be increased to 95 %, with 94 % diastereoselectivity for (±)-menthol. The low initial pressure minimises the rates of competing hydrogenation reactions to byproducts such as citronellol and 3,7-dimethyloctanol.

- Photoresponsive Cyclodextrin-Covered Nanocontainers and Their Sol-Gel Transition Induced by Molecular Recognition
  Park, C.; Lee, K.; Kim, C. *Angew. Chem. Int. Ed.* **2009**, *48*, 1275 –1278.
  Abstract:



Springing the trap: Cyclodextrin-covered mesoporous silica nanoparticles with photocleavable linkers exhibit photoinduced release characteristics and a sol-gel transition that is induced by molecular recognition (see picture). Upon exposure to UV light, the guest molecules were released from the pore by removal of the CD "gatekeeper", which was linked on the surface of the silica nanoparticle through a photocleavable *o*-nitrobenzyl ester moiety.

- Dynamic Combinatorial Evolution within Self-Replicating Supramolecular Assemblies
  Nguyen, R.; Allouche, L.; Buhler, E.; Giuseppone, N. *Angew. Chem. Int. Ed.* **2009**, *48*, 1093 – 1096.
  Abstract:



Survival of the fittest: Self-assemblies made of dynamic block copolymers (dynablocks) can self-replicate by catalyzing the formation of their own building blocks. Moreover, in competition experiments, the differential thermodynamic stabilities and autocatalytic efficiencies of these self-assemblies lead to sigmoid growth of the most efficient self-replicator and to depletion of its competitors.