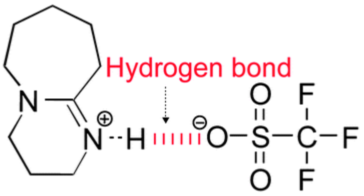
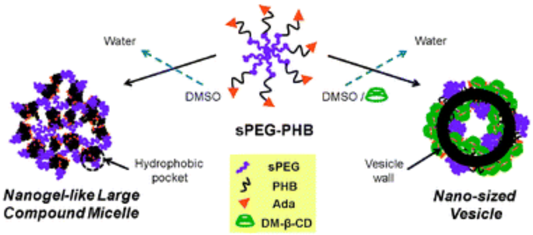
- Hydrogen bonds in protic ionic liquids and their correlation with physicochemical properties
  Miran, M. S.; Kinoshita, H.; Yasuda, T.; Susan, M. A. B. H.; Watanabe, M. *Chem. Commun.*, **2011**, *47*, 12676-12678.
  Abstract:



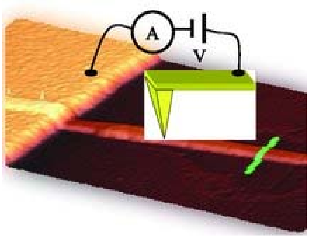
The temperature dependence of the N–H proton chemical shift in protic ionic liquids (PILs) and FT-IR spectra of the N–H bonds indicated the presence of strong hydrogen bonds between the protonated cation and the anion, depending on the ΔpK_a of the constituent acid and base, and their successive breaking with temperature, which may explain the characteristic properties of PILs such as relatively low ionicity and its decrease with temperature.

- Amphiphilic star-block copolymers and supramolecular transformation of nanogel-like micelles to nanovesicles,
  Zhu, J.; Liu, K.L.; Zhang, Z.; Zhang X.; Li, J. *Chem. Commun*. **2011**, *47,* 12849-12851.
  Abstract:



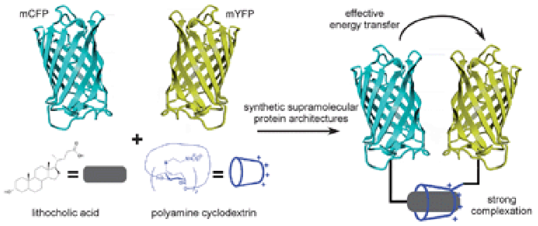
Amphiphilic star-block copolymers based on poly(3-hydroxybutyrate) with adamantyl end-functionalization were synthesized *via* anionic ring-opening polymerization and alkyne–azide “Click Chemistry” coupling. In aqueous medium, the copolymers self-assembled into nanogel-like large compound micelles, and transformed into vesicular nanostructures under the direction of host–guest interaction between the adamantyl end and dimethyl-β-cyclodextrin.

- Coordination Polymers for Nanoelectronics
  Gómez-Herrero, J.; Zamora, F. *Adv. Mat.* **2011***, 23,* 5311–5317.
  Abstract:



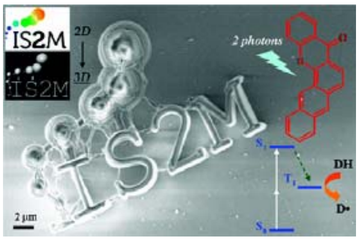
We review recent progress in the potential use of coordination polymers as molecular wires for nanoelectronics. To this end we review some basic aspects of these materials including synthesis and properties in the bulk scale; processability towards the formation of nanoscale structures and seminal works on electrical transport of coordination polymers. Finally, we summarize some of the perspectives in this field.

- Strong supramolecular control over protein self-assembly using a polyamine decorated β cyclodextrin as synthetic recognition element.
  Uhlenheuer, D.A.; Milroy, L.G.; Neirynck, P.; Brunsveld, L. *J. Mater. Chem.* **2011,** *21*, 18919-18922.
  <u>Abstract:</u>



The supramolecular host molecule heptakis-[6-deoxy-6-(2-aminoethylsulfanyl)] -β-cyclodextrin provides strong control over protein self-assembly in synthetic supramolecular protein constructs. Mono-functionalization of this modified β-cyclodextrin with a cysteine residue allows for site-selective synthetic conjugation to a protein and formation of a highly stable synthetic protein complex with a lithocholic acid conjugated protein as the interaction partner.

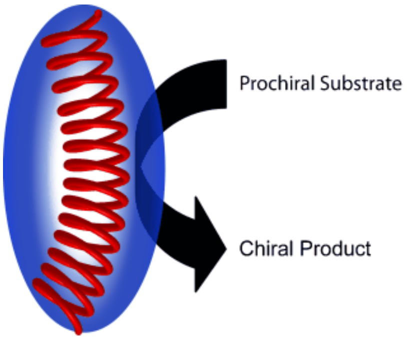
- Enhancement of the Two-Photon Initiating Efficiency of a Thioxanthone Derivative through a Chevron-Shaped Architecture.
  Malval, J.-P. ; Jin, M.; Morlet-Savary, F.; Chaumeil, H.; Defoin, A.; Soppera, O.; Scheul, T.; Bouriau, M.; Baldeck, P.L. *Chem. Mater*. **2011**, *23,* 3411-3420.
  <u>Abstract:</u>



We investigated the one- and two-photon excitation properties of a new hybrid anthracenethioxanthone (ANTX) system, which was assembled into a chevron-shaped molecular architecture. Such a geometrical association first preserves the high efficiency of the free radical photo initiator and leads, in the same time, to a strong increase in the two-photon absorption (2PA) cross section by more than a factor of 30 as compared to thioxanthone (TX). A four-state model was required to fit the 2PA spectrum of ANTX, which clearly undergoes a strong enhancement in the low-frequency region. As a consequence, ANTX constitutes a suitable two-photon initiating chromophore with a much higher efficiency as TX used as reference. At λ_{exc} = 710 nm for instance, we showed that the two-photon polymerization threshold of ANTX is five times lower with respect to that of TX. Additionally, we demonstrated by the fabrication of three-dimensional microstructures that this new hybrid system remains two-photon activable when excited at wavelengths near its one-photon absorption region as suggested by the sum-overstates model. We also show that this new two-photon initiator exhibits a higher reactivity than a diaminofluorene derivative, which is commonly used in two-photon polymerization.

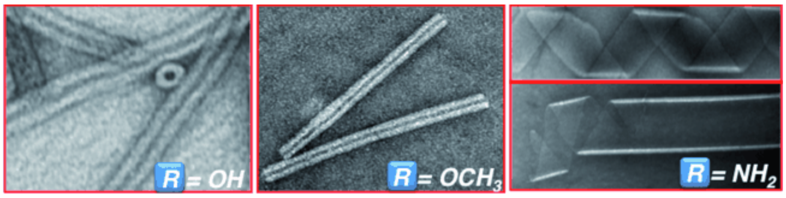
- Asymetric Catalysis with Helical Polymers
  Megens, R. P.; Roelfes, G. *Chem. Eur. J.* **2011**, *17*, 8514-8523.

Abstract:



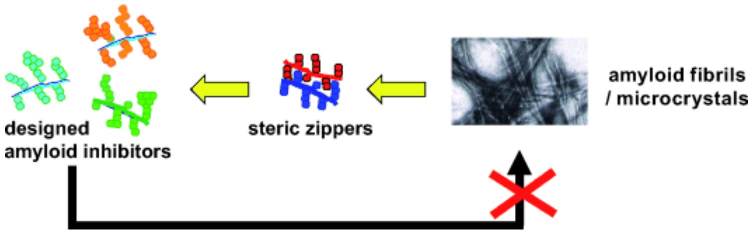
Inspired by nature, the use of helical biopolymer catalysts has emerged over the last years as a new approach to asymmetric catalysis. In this Concept article the various approaches and designs and their application in asymmetric catalysis will be discussed.

- Aqueous Self-Assembly of L-Lysine-Based Amphiphiles into 1D n-Type Nanotube
  Shao, H.; Gao, M.; Kim, S. H.; Jaroniec, C. P.; Parquette, J. R. *Chem. Eur. J.* **2011**, *17*, 12882-12885.
  Abstract:



Assembly call: The 1D self-assembly of tube-forming NDI–lysine amphiphiles in water is described. Nanotubes formed from an acid or ester give nanotubes with small inner diameters of 4–5 nm, whereas the corresponding amide coils into nanotubes with diameters ranging from 100–200 nm (see TEM images). Spectroscopic measurements indicate the presence of highly ordered, homogeneous structures with significant π–π interactions.

- Terminating the Amyloid Zipper by Design
  Kapurniotu, A. *Angew. Chem. Int. Ed.* **2011**, *50,* 11293–11294.
  Abstract:

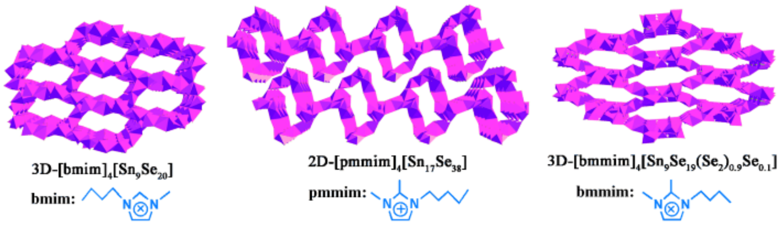


Zip code: A potentially general, computational design approach has been used to devise peptide inhibitors of protein aggregation into amyloid fibrils. The atomic structures of “steric zippers”, which are formed by short fibril-forming segments of the amyloidogenic proteins, serve as templates. The validity of the approach is demonstrated by the design of inhibitors of amyloid formation associated with Alzheimer's disease pathology and HIV infectivity.

- Crystalline Open-Framework Selenidostannates Synthesized in Ionic Liquids

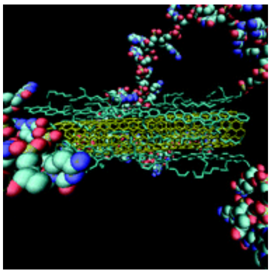
Li, J. R.; Xie, Z. L.; He, X. W.; Li, L. H.; Huang, X.Y. *Angew. Chem. Int. Ed.* **2011**, *50,* 11395–11399.

Abstract:



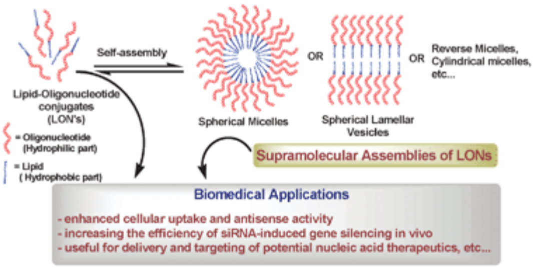
Ready to direct: Crystalline selenidostannates were synthesized in imidazolium-based ionic liquids with a small amount of hydrazine monohydrate as additive (see scheme). They are the first open-framework chalcogenides structurally directed by imidazolium cations and are inaccessible by traditional methods.

- Nucleic acid amphiphiles : synthesis and self-assembled nanostructures
  Kwak, M.; Herrmann, A. *Chem. Soc. Rev.* **2011**, *40*, 5745-5755.
  Abstract:



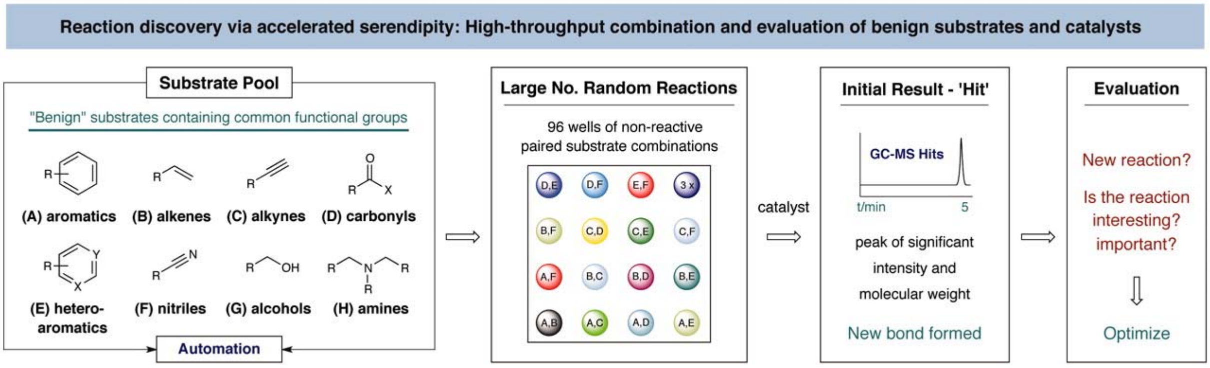
This review provides an overview of a relatively new class of bio-conjugates, DNA amphiphiles, which consist of oligonucleotides covalently bonded to synthetic hydrophobic units. The reader will find the basic principles for the structural design and preparation methods of the materials. Moreover, the self-assembly into superstructures of higher order will be highlighted. Finally, some potential applications will be described.

- Hybrid lipid oligonucleotide conjugates: synthesis, self-assemblies and biomedical applications
  Patwa, A.; Gissot, A.; Bestel, I.; Barthélémy, P. *Chem. Soc. Rev.* **2011,** *40*, 5844-5854.
  Abstract:



Hybrid lipid oligonucleotide conjugates are finding more and more biotechnological applications. This short *critical review* highlights their synthesis, supramolecular organization as well as their applications in the field of biotechnology (111 references).

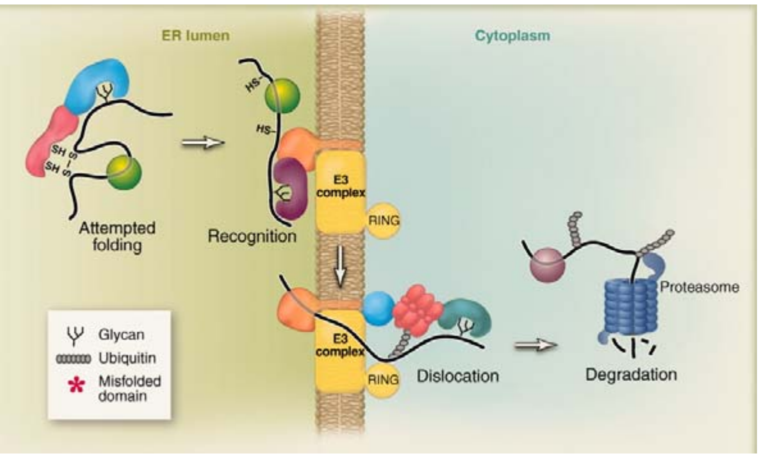
- Discovery of an α-Amino C–H Arylation Reaction Using the Strategy of Accelerated Serendipity
  McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science* **2011**, *334,* 1114-1117.
  Abstract:



Serendipity has long been a welcome yet elusive phenomenon in the advancement of chemistry. We sought to exploit serendipity as a means of rapidly identifying unanticipated chemical transformations. By using a high-throughput, automated workflow and evaluating a large number of random reactions, we have discovered a photoredox-catalyzed C–H arylation reaction for the construction of benzylic amines, an important structural motif within pharmaceutical compounds that is not readily accessed via simple substrates. The mechanism directly couples tertiary amines with cyanoaromatics by using mild and operationally trivial conditions.

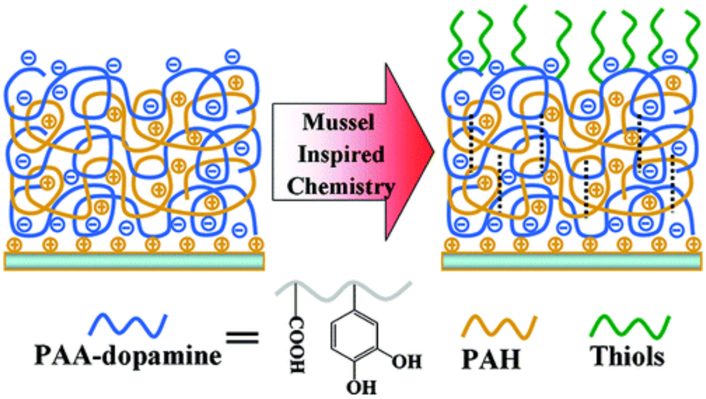
- Road to Ruin: Targeting Proteins for Degradation in the Endoplasmic Reticulum
  Smith, M. H.; Ploegh, H. L.; Weissman, J. S. *Science* **2011**, *334,* 1086-1090.

  Abstract:



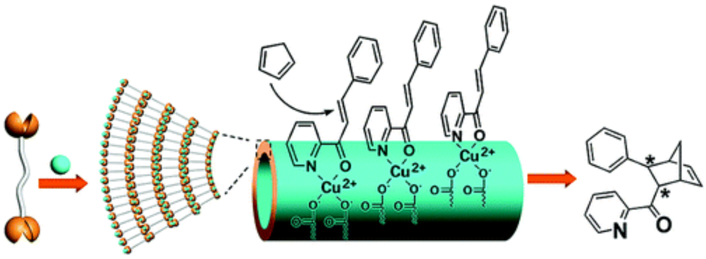
Some nascent proteins that fold within the endoplasmic reticulum (ER) never reach their native state. Misfolded proteins are removed from the folding machinery, dislocated from the ER into the cytosol, and degraded in a series of pathways collectively referred to as ER-associated degradation (ERAD). Distinct ERAD pathways centered on different E3 ubiquitin ligases survey the range of potential substrates. We now know many of the components of the ERAD machinery and pathways used to detect substrates and target them for degradation. Much less is known about the features used to identify terminally misfolded conformations and the broader role of these pathways in regulating protein half-lives.

- Mussel-Inspired Chemistry for Robust and Surface-Modifiable Multilayer Films
  Wu, J.; Zhang, L.; Wang, Y.; Long, Y.; Gao, H.; Zhang, X.; Zhao, N.; Cai, Y.; Xu, J. *Langmuir* **2011**, *27,* 13684-13691.
  Abstract:



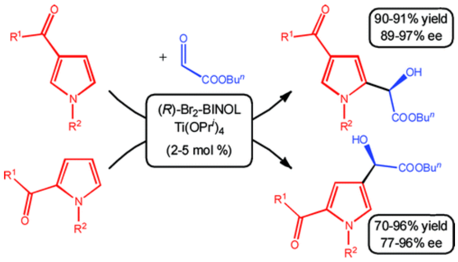
In this article, we report a bioinspired approach to preparing stable, functional multilayer films by the integration of mussel-inspired catechol oxidative chemistry into a layer-by-layer (LbL) assembly. A polyanion of poly(acrylic acid-*g*-dopamine) (PAA-dopamine) bearing catechol groups, a mussel adhesive protein-mimetic polymer, was synthesized as the building block for LbL assembly with poly(allylamine hydrochloride) (PAH). The oxidization of the incorporated catechol group under mild oxidative condition yields *o*-quinone, which exhibits high reactivity with amine and catechol, thus endowing the chemical covalence and retaining the assembled morphology of multilayer films. The cross-linked films showed excellent stability even in extremely acidic, basic, and highly concentrated aqueous salt solutions. The efficient chemical cross-linking allows for the production of intact free-standing films without using a sacrificial layer. Moreover, thiol-modified multilayer films with good stability were exploited by a combination of thiols-catechol addition and then oxidative cross-linking. The outstanding stability under harsh conditions and the facile functionalization of the PAA-dopamine/PAH multilayer films make them attractive for barriers, separation, and biomedical devices.

- Self-Assembly of Copper(II) Ion-Mediated Nanotube and Its Supramolecular Chiral Catalytic Behavior
  Jin, Q.; Zhang, L.; Cao, H.; Wang, T.; Zhu, X.; Jiang, J.; Liu, M. *Langmuir* **2011**, *27,* 13847-13853.
  Abstract:



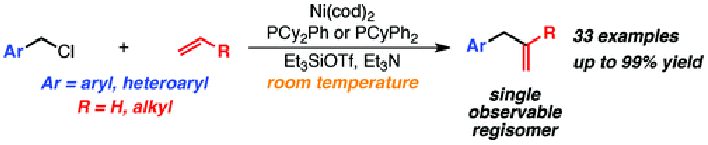
Self-assembly of several low-molecular-weight l-glutamic acid-based gelators, which individually formed helical nanotube or nanofiber structures, was investigated in the presence of Cu^{2+} ion. It was found that, when Cu^{2+} was added into the system, the self-assembly manner changed significantly. Only in the case of bolaamphiphilic glutamic acid, *N,N'*-hexadecanedioyl-di-l-glutamic acid (L-HDGA), were the hydrogel formation as well as the nanotube structures maintained. The addition of Cu^{2+} ion caused a transition from monolayer nanotube of L-HDGA to a multilayer nanotube with the thickness of the tubular wall about 10 nm. For the other amphiphiles, the gel was destroyed and nanofiber structures were mainly formed. The formed Cu^{2+}-containing nanostructures can function as an asymmetric catalyst for Diels–Alder cycloaddition between cyclopentadiene and aza-chalcone. In comparison with the other Cu^{2+}-containing nanostructures, the Cu^{2+}-mediated nanotube structure showed not only accelerated reaction rate, but enhanced enantiomeric selectivity. It was suggested that, through the Cu^{2+} mediated nanotube formation, the substrate molecules could be anchored on the nanotube surfaces and produced a stereochemically favored alignment. When adducts reacted with the substrate, both the enantiomeric selectivity and the reaction rate were increased. Since the Cu^{2+}-mediated nanotube can be fabricated easily and in large amount, the work opened a new way to perform efficient chiral catalysis through the supramolecular gel.

- Enantioselective Friedel–Crafts Reaction of Acylpyrroles with Glyoxylates Catalyzed by BINOL–Ti(IV) Complexes
  Majer, J.; Kwiatkowski, P.; Jurczak, J. *Org. Lett.* **2011**, *13,* 5944–5947.
  Abstract:



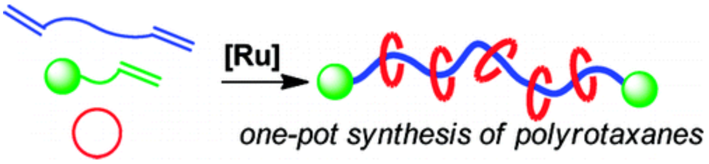
We report the first efficient enantioselective Friedel–Crafts hydroxyalkylation of pyrroles having one electron-withdrawing group at the α, β or *N*-positions with alkyl glyoxylates catalyzed by readily available chiral BINOL–Ti(IV) complexes (1–5 mol %). The reaction regioselectively led to the desired pyrrole-hydroxyacetic acid derivatives with good yields (70–96%) and enantiomeric excesses up to 96%, and is applicable in multigram scale with low loading of the catalyst (1 mol %).

- Nickel-Catalyzed Heck-Type Reactions of Benzyl Chlorides and Simple Olefins
  Matsubara, R.; Gutierrez, A. C.; Jamison, T. F. *J. Am. Chem. Soc.* **2011,** *133,* 19020-19023.
  Abstract:



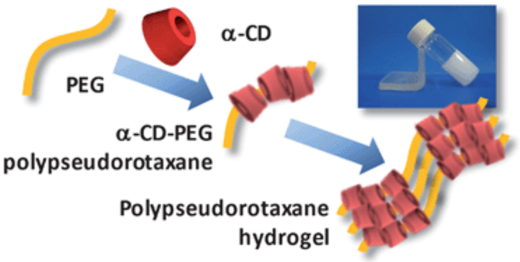
Nickel-catalyzed intermolecular benzylation and heterobenzylation of unactivated alkenes to provide functionalized allylbenzene derivatives are described. A wide range of both the benzyl chloride and alkene coupling partners are tolerated. In contrast to analogous palladium-catalyzed variants of this process, all reactions described herein employ electronically unbiased aliphatic olefins (including ethylene), proceed at room temperature, and provide 1,1-disubstituted olefins over the more commonly observed 1,2-disubstituted olefins with very high selectivity.

- One-Pot Synthesis of Polyrotaxanes via Acyclic Diene Metathesis Polymerization of Supramolecular Monomers
  Momčilović, N.; Clark, P. G.; Boydston, A. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011,** *133*, 19087-19089.
  <u>Abstract:</u>



A one-pot synthesis of polyrotaxanes has been developed. The method employs a supramolecular monomer comprising a polymerizable ammonium salt and crown ether, in combination with dynamic ADMet polymerization. Ultimately, highly efficient complexation, polymerization, and end-capping were accomplished in a single operation to yield polyrotaxanes with M_w up to 19.3 kDa and >80% of the repeat units being complexed.

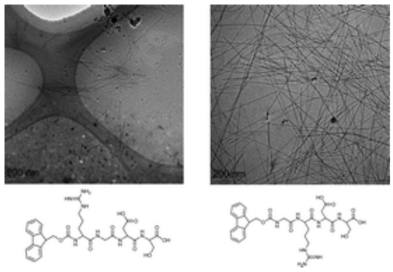
- Supramolecular hydrogels based on cyclodextrin–polymer polypseudorotaxanes: materials design and hydrogel properties
  Li Liu, K.; Zhang, Z.; Li J. *Soft Matter* **2011**, *7*, 11290-11297.
  <u>Abstract:</u>



Supramolecular hydrogels formed by cyclodextrins (CDs) and polymers based on polypseudorotaxane formation have attracted great interest because of their potential applications as injectable hydrogel drug delivery systems due to their thixotropic nature and biocompatibility. Recent advancements in this area have led to improvements in the hydrogel rheological and drug delivery properties, marking a step forward towards practical applications. The development of novel CD–polypseudorotaxane hydrogels with new stimuli-responsive properties is another important progress in this area. These new developments are highlighted here from the perspective of materials design and hydrogel properties together with a state-of-the-art understanding on CD–polypseudorotaxane hydrogel formation.

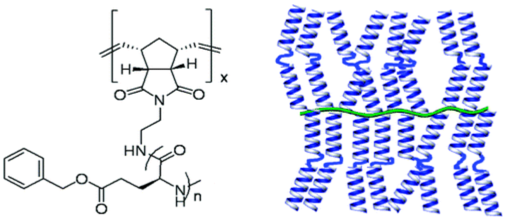
- Self-assembly of Fmoc-tetrapeptides based on the RGDS cell adhesion motif
  Castelletto,V.; Moulton, C. M.; Cheng, G.; Hamley, I. W.; Hicks, M. R.; Rodger, A.; López-Pérez, D. E.; Revilla-López G.; Alemán C. *Soft Matter* **2011**, *7*, 11405-11415.

Abstract:



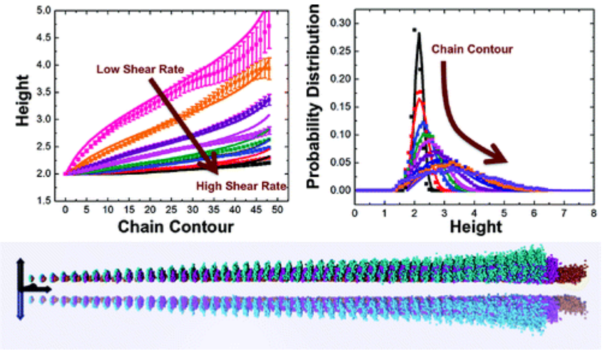
Self-assembly in aqueous solution has been investigated for two Fmoc [Fmoc = N-(fluorenyl)-9-methoxycarbonyl] tetrapeptides comprising the RGDS cell adhesion motif from fibronectin or the scrambled sequence GRDS. The hydrophobic Fmoc unit confers amphiphilicity on the molecules, and introduces aromatic stacking interactions. Circular dichroism and FTIR spectroscopy show that the self-assembly of both peptides at low concentration is dominated by interactions among Fmoc units, although Fmoc-GRDS shows β-sheet features, at lower concentration than Fmoc-RGDS. Fibre X-ray diffraction indicates β-sheet formation by both peptides at sufficiently high concentration. Strong alignment effects are revealed by linear dichroism experiments for Fmoc-GRDS. Cryo-TEM and small-angle X-ray scattering (SAXS) reveal that both samples form fibrils with a diameter of approximately 10 nm. Both Fmoc-tetrapeptides form self-supporting hydrogels at sufficiently high concentration. Dynamic shear rheometry enabled measurements of the moduli for the Fmoc-GRDS hydrogel, however syneresis was observed for the Fmoc-RGDS hydrogel which was significantly less stable to shear. Molecular dynamics computer simulations were carried out considering parallel and antiparallel β-sheet configurations of systems containing 7 and 21 molecules of Fmoc-RGDS or Fmoc-GRDS, the results being analyzed in terms of both intermolecular structural parameters and energy contributions.

- Interrupted Helical Structure of Grafted Polypeptides in Brush-Like Macromolecules
  Wang, J.; Lu, H.; Ren, Y.; Zhang, Y.; Morton, M.; Cheng, J.; Lin, Y. *Macromolecules* **2011,** *44,* 8699–8708.
  Abstact:



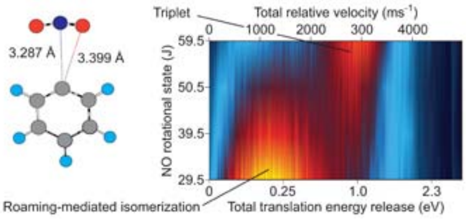
Brush-like polymers are a type of graft polymers with densely and regularly spaced side chains. Their unique topologies and large sizes afforded a number of potential applications in nanotechnology. Incorporating helical polypeptides as grafted chains in brush polymers may allow for the construction of large macromolecules with structurally well-defined, rod-like domains. However, due to a congested local environment in brush polymers, the conformational structure of grafted polypeptides can deviate from the “rigid-rod” α-helical structure observed in homopolypeptides. Because of synthetic challenges, the effect of macromolecular environments on the conformational structures of grafted polypeptides has not been systematically studied in brush polymers. Here we synthesized a small library of polynorbornene-g-poly(γ-benzyl-l-glutamate) (PN-g-PBLG) with variable PN, PBLG lengths and grafting densities, and we studied solvent induced helix–coil transition of grafted PBLGs in these brush polymers to explore their specific conformational structures. Instead of forming rigid-rod α-helices in helicogenic solvents, the grafted PBLGs in PN-g-PBLG, especially those with high grafting density and high molecular weights (MWs), adopt interrupted helical structures that can be represented by a "broken rod" model, which was also confirmed by the nuclear overhauser enhancement spectroscopy (NOESY) experiments. The behavior also exists in other types of grafted polypeptides in brush polymers, e.g., PN-g-poly(ε-benzyloxycarbonyl-l-lysine) (PN-g-PZLL). These findings and the structural analysis methods we developed in this study provide the guidance to the rational design and characterization of polypeptide-containing macromolecules with complex architectures.

- Theory of Tethered Polymers in Shear Flow: The Strong Stretching Limit
  Sing, C. E.; Katz, A. *Macromolecules* **2011**, *44*, 9020–9028.
  Abstract:



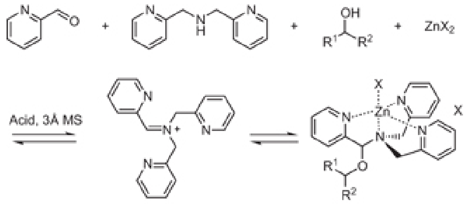
In the present article, we use simulation and theory to understand the case of flexible and semiflexible tethered polymers in the limit of high shear flows and consequently near-full extension of the chains. We adopt a random-walk picture along the axis of the polymer, which in combination with a statistical mechanical description of perturbations along the chain contour allows us to fully characterize the geometry of the polymer chain without any fit parameters. Incorporation of hydrodynamic interactions is also investigated, with the hydrodynamic lift force inducing changes in the chain equilibrium structure near the tether point that could have implications for adsorption and desorption kinetics.

- Roaming-mediated isomerization in the photodissociation of nitrobenzene
  Hause, M. L.; Herath, N.; Zhu, R.; Lin, M.C.; Suits, A. G. *Nature Chem.* **2011**, *3*, 932-937.
  Abstract:



Roaming reactions comprise a new class of reaction in which a molecule undergoes frustrated dissociation to radicals, followed by an intramolecular abstraction reaction. Nitro compounds have long been known to dissociate to give NO as a major product. However, rates based upon isomerization via calculated tight transition states are implausibly slow, so the key dissociation pathway for this important class of molecules remains obscure. Here, we present an imaging study of the photodissociation of nitrobenzene with state-specific detection of the resulting NO products. We observe a bimodal translational energy distribution in which the slow products are formed with low NO rotational excitation, and the fast component is associated with high rotational excitation. High-level *ab initio* calculations identified a ‘roaming-type’ saddle point on the ground state. Branching ratio calculations then show that thermal dissociation of nitrobenzene is dominated by ‘roaming-mediated isomerization’ to phenyl nitrite, which subsequently decomposes to give C_6H_5O + NO.

- Dynamic multi-component covalent assembly for the reversible binding of secondary alcohols and chirality sensing
  You, L.; Berman, J. S.; Anslyn, E. V. *Nature Chem.* **2011**, *3*, 943-948.
  Abstract:



Reversible covalent bonding is often used for the creation of novel supramolecular structures, multi-component assemblies and sensing ensembles. Despite the remarkable success of dynamic covalent systems, the reversible binding of a mono-alcohol with high strength is challenging. Here, we show that a strategy of carbonyl activation and hemiaminal ether stabilization can be embodied in a four-component reversible assembly that creates a tetradentate ligand and incorporates secondary alcohols with exceptionally high affinity. Evidence is presented that the intermediate leading to binding and exchange of alcohols is an iminium ion. To demonstrate the use of this assembly process we also explored chirality sensing and enantiomeric excess determinations. An induced twist in the ligand by a chiral mono-ol results in large Cotton effects in the circular dichroism spectra indicative of the handedness of the alcohol. The strategy revealed in this study should prove broadly applicable for the incorporation of alcohols into supramolecular architecture construction.