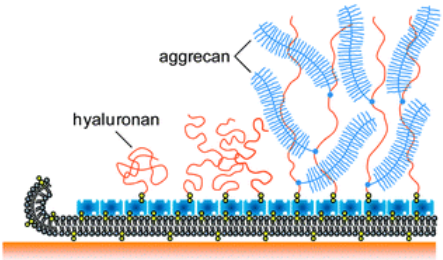
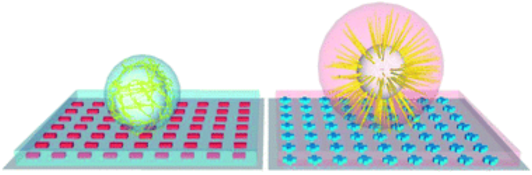
- Self-assembly and elasticity of hierarchical proteoglycan–hyaluronan brushes
  Attilli, S.; Richter, R. P. *Soft Matter* **2013**, *9,* 10473-10483.
  Abstract:



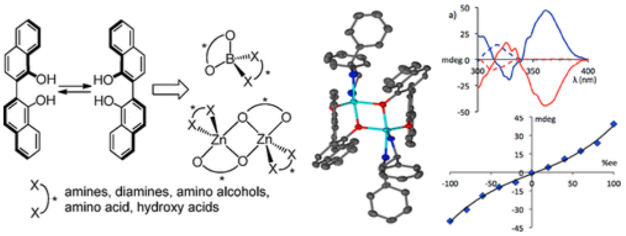
Spatially confined yet strongly hydrated assemblies made from the proteoglycan aggrecan and the polysaccharide hyaluronan (HA) are major, functionally important components of the pericellular space around chondrocytes, and in cartilage. To better understand, how mechanical properties arise from the supramolecular structure and dynamics of such assemblies, we have studied the effect of aggrecan on the physico-chemical properties of well-defined, planar HA brushes. From interaction studies by quartz crystal microbalance with dissipation monitoring and spectroscopic ellipsometry, and compression studies by combined colloidal probe atomic force/reflection interference contrast microscopy, we find that aggrecan readily intercalates into HA brushes in a reversible manner. Aggrecan induces a drastic swelling of HA brushes, generating self-assembled films of several micrometers in thickness that are highly hydrated (>99%), elastic and very soft. The Young modulus in the linear compression regime is well below 100 Pa, and reaches several kPa at strong compression. The implications of these findings for biological function are discussed.

- The effect of electric fields on bacterial attachment to conductive surfaces
  Gall, I.; Herzberg, M.; Oren, Y. *Soft Matter* **2013***, 9,* 2443-2452.
  Abstract:



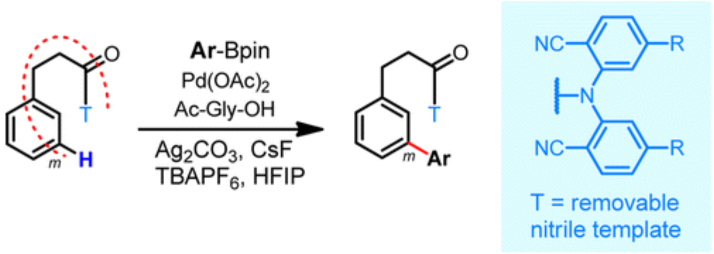
Bacterial adhesion has been studied in various conditions. The bactericidal effect of strong electric voltages has been mainly tested within the context of preventing device-related infections in hospital environments. Little evidence is found in the literature on the mechanism of bacterial deposition as a function of an applied electric field. In this study, we assumed that an electric field, which was applied perpendicularly to the flow of a bacterial suspension, might impact the electrostatic energy barrier between the negatively charged bacterial cell and the positively charged electrode substrate. Experiments were carried out with a QCM-D electro-chemical module which allowed monitoring the adhered mass as well as the dissipation factor, while a bacterial suspension was passed through the module in a diffusion dominated flow regime and while an electric field was applied perpendicularly to the flow of the suspension. A Pseudomonas fluorescens strain was used in order to detect and estimate any bacterial adhesion on the electrode surface. While the results confirmed that a decrease of the recorded resonance frequency was in direct proportion to the amount of adhered bacteria (estimated by a visual control of the bacterial signal on the electrode sensor at the end of each experiment), the change in the resonance frequency as a function of the applied electric potential was rather counter-intuitive: with negative potential the rate of bacterial adhesion was faster and steadier than with a positive electric potential, when the bacterial rate of adhesion tended to level off. Moreover, analyses of the measured dissipation to the measured frequency shifts (ΔD/Δf) during the deposition experiment, which indicate the fluidic character of the adhered layer of bacteria, revealed that with negative electric potential the bacterial cells were rigidly connected, while with positive electric potentials the cells were rather loosely bound to the electrode. The measured data suggested that the applied electric potential might have an impact on the conformation of the surface appendages on the bacterial cell surface of P. fluorescens, causing a state of steric repulsion with an extended conformation induced by positive electric potentials, and a state of entangled conformations induced by negative potentials, which allowed the cells to overcome the electrostatic energy barrier.

- Chirality Sensing of Amines, Diamines, Amino Acids, Amino Alcohols, and α-Hydroxy Acids with a Single Probe
  Bentley, K. W.; Nam, Y. G.; Murphy, J. M.; Wolf, C. *J. Am. Chem. Soc.* **2013**, *135*, 18052-18055.
  Abstract:



A stereodynamic probe for determination of the absolute configuration and enantiomeric composition of chiral amines, diamines, amino alcohols, amino acids, and α-hydroxy carboxylic acids is described. The chirality sensing is based on spontaneous asymmetric transformation of the first kind with stereolabile binaphtholate boron and zinc complexes. The substrate binding and chiral amplification processes yield a distinctive chiroptical sensor output at high wavelength that can be used for rapid and accurate ee detection of minute sample amounts.

- Cross-Coupling of Remote meta-C–H Bonds Directed by a U-Shaped Template
  Wan, L.; Dastbaravardeh, N.; Li, G.; Yu, J.-Q. *J. Am. Chem. Soc.* **2013**, *135*, 18056-18059.
  Abstract:

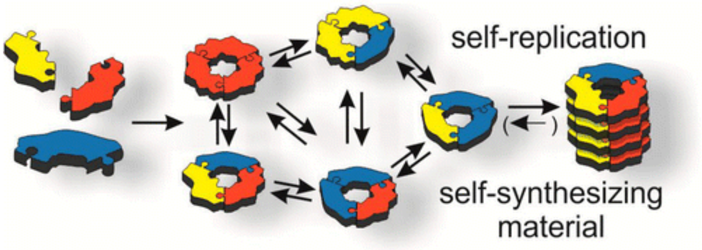


meta-C–H arylation and methylation of 3-phenylpropanoic acid and phenolic derivatives were developed using an easily removable nitrile template. The combination of a weakly coordinating U-shaped template and mono-protected amino acid ligand was crucial for the cross-coupling of C–H bonds with organoborons.

- Uncovering the Selection Criteria for the Emergence of Multi-Building-Block Replicators from Dynamic Combinatorial Libraries

Malakoutikhah, M.; Peyralans, J.-P. ; Colomb-Delsuc, M.; Fanlo-Virgós, H.; Stuart, M. C. A.; Otto, S. J. *Am. Chem. Soc.* **2013**, *135*, 18406–18417.

Abstract:

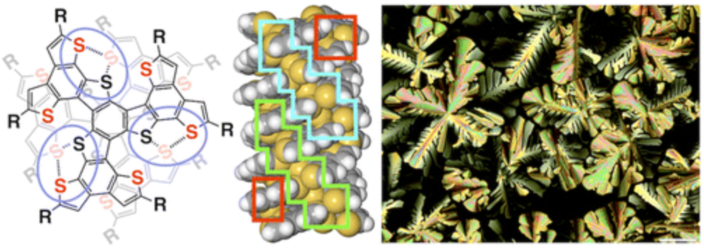


A family of self-replicating macrocycles was developed using dynamic combinatorial chemistry. Replication is driven by self-assembly of the replicators into fibrils and relies critically on mechanically induced fibril fragmentation. Analysis of separate dynamic combinatorial libraries made from one of six peptide-functionalized building blocks of different hydrophobicity revealed two selection criteria that govern the emergence of replicators from these systems. First, the replicators need to have a critical macrocycle size that endows them with sufficient multivalency to enable their self-assembly into fibrils. Second, efficient replication occurs only for library members that are of low abundance in the absence of a replication pathway. This work has led to spontaneous emergence of replicators with unrivalled structural complexity, being built from up to eight identical subunits and reaching a MW of up to 5.6 kDa. The insights obtained in this work provide valuable guidance that should facilitate future discovery of new complex self-replicating molecules. They may also assist in the development of new self-synthesizing materials, where self-assembly drives the synthesis of the very molecules that self-assemble. To illustrate the potential of this concept, the present system enables access to self-assembling materials made from self-synthesizing macrocycles with tunable ring size ranging from trimers to octamers.

- Propeller-Shaped Fused Oligothiophenes: A Remarkable Effect of the Topology of Sulfur Atoms on Columnar Stacking

  Xiao, Q.; Sakurai, T.; Fukino, T.; Akaike, K.; Honsho, Y.; Saeki, A.; Seki, S.; Kato, K.; Takata, M.; Aida, T. *J. Am. Chem. Soc.* **2013**, *135*, 18268–18271.

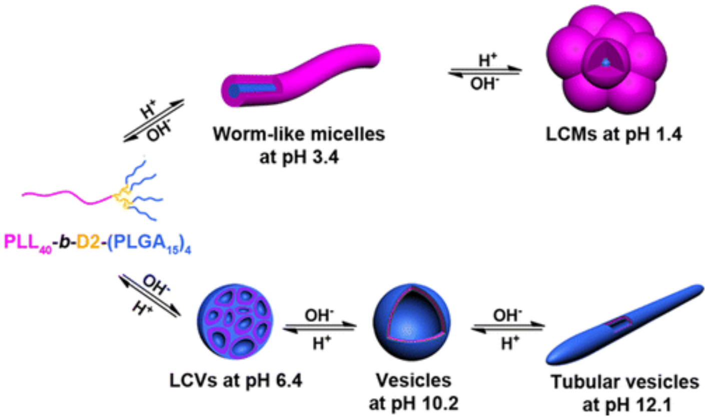
  Abstract:



Helical LC Column of Stacked **F9T$_{endo}$** *via* S–S Contacts

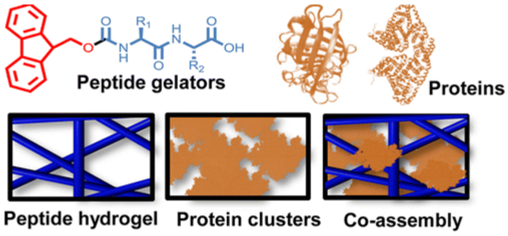
Propeller-shaped regioisomers of fused oligothiophenes F9Tendo, F9Tanti, and F9Texo were successfully synthesized. DFT calculations indicated that their core parts are distorted from planarity due to intramolecular steric repulsions involving large sulfur atoms. In contrast with soft crystalline F9Tanti and F9Texo, F9Tendo self-assembles into a hexagonal columnar liquid crystal (Colh LC), displaying a clear X-ray diffraction (XRD) due to its stacked π-conjugated core. In each LC column, well-organized intermolecular S–S contacts are developed triple-helically along the columnar axis with a helical pitch of 4.04 nm. Among LC semiconductors reported to date, Colh LC F9Tendo displays a top-class charge-carrier mobility (0.18 cm2 V–1 s–1) with a distinct ambipolar character featuring well-balanced hole and electron mobilities. A thin film, prepared by mixing F9Tendo with soluble fullerene PCBM, shows a photovoltaic response, when the fullerene content is large enough to compensate a small absorptivity of F9Tendo for visible light.

- Synthesis and pH-Responsive “Schizophrenic” Aggregation of a Linear-Dendron-Like Polyampholyte Based on Oppositely Charged Polypeptides
  Chen, L.; Chen, T.; Fang, W.; Wen, Y.; Lin, S.; Lin, J.; Cai, C. *Biomacromolecules* **2013**, *14*, 4320–4330.
  Abstract:



A novel linear-dendron-like polyampholyte, poly(l-lysine)-*b*-D2-poly(l-glutamic acid) [PLL-*b*-D2-$(PLGA)_4$], where D2 is the second generation of poly(amido amine), was prepared by hydrolyzing poly(ε-benzyloxycarbonyl-l-lysine)-*b*-D2-poly(γ-benzyl-l-glutamate) copolymer which was synthesized via a combination of ring-opening polymerization and click chemistry. The pH-responsive self-assembly behaviors of PLL-*b*-D2-$(PLGA)_4$ were investigated in detail. It is found that PLL-*b*-D2-$(PLGA)_4$ can self-assemble into PLGA-core aggregates at acidic pH and PLL-core aggregates at alkaline pH, which was accompanied with the coil-to-helix conformational transition of PLGA and PLL segments, respectively. The self-assembled aggregates with various morphologies, such as large compound micelles, worm-like micelles, large compound vesicles, simple vesicles, and rigid tubular structures have been obtained in “schizophrenic” aggregation process with simply increasing the solution pH. The hierarchical assembled fractal structures of PLL-*b*-D2-$(PLGA)_4$ were observed during the solvent evaporation at high pH value.

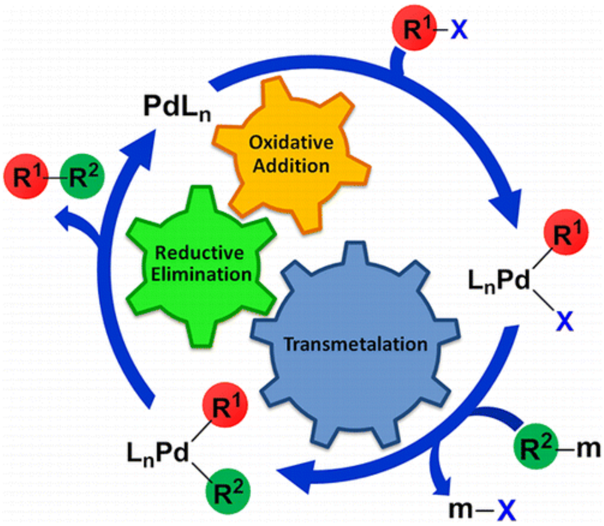
- Cooperative Self-Assembly of Peptide Gelators and Proteins
  Javid, N.; Roy, S.; Zelzer, M.; Yang, Z.; Sefcik, J.; Ulijn, R. V. *Biomacromolecules* **2013**, *14*, 4368–4376.
  Abstract:



Molecular self-assembly provides a versatile route for the production of nanoscale materials for medical and technological applications. Herein, we demonstrate that the cooperative self-assembly of amphiphilic small molecules and proteins can have drastic effects on supramolecular

nanostructuring of resulting materials. We report that mesoscale, fractal-like clusters of proteins form at concentrations that are orders of magnitude lower compared to those usually associated with molecular crowding at room temperature. These protein clusters have pronounced effects on the molecular self-assembly of aromatic peptide amphiphiles (fluorenylmethoxycarbonyl-dipeptides), resulting in a reversal of chiral organization and enhanced order through templating and binding. Moreover, the morphological and mechanical properties of the resultant nanostructured gels can be controlled by the cooperative self-assembly of peptides and protein fractal clusters, having implications for biomedical applications where proteins and peptides are both present. In addition, fundamental insights into cooperative interplay of molecular interactions and confinement by clusters of chiral macromolecules is relevant to gaining understanding of the molecular mechanisms of relevance to the origin of life and development of synthetic mimics of living systems.

- Computational Perspective on Pd-Catalyzed C–C Cross-Coupling Reaction Mechanisms
  García-Melchor, M.; Braga, A. A. C.; Lledós, A.; Ujaque, G.; Maseras, F. *Acc. Chem. Res.* **2013**, *46*, 2626–2634.
  <u>Abstract:</u>

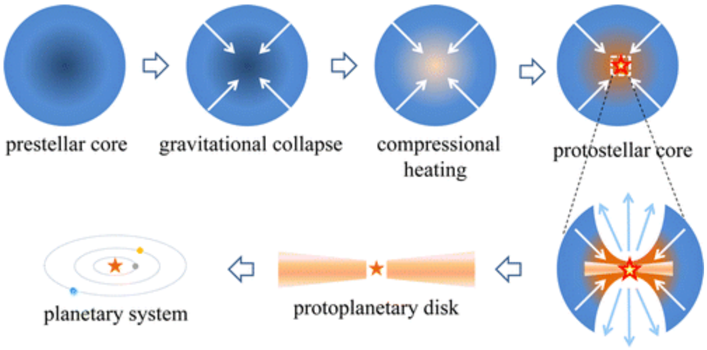


Palladium-catalyzed C–C cross-coupling reactions (Suzuki–Miyaura, Negishi,Stille, Sonogashira, etc.) are among the most useful reactions in modern organic synthesis because of their wide scope and selectivity under mild conditions. The many steps involved and the availability of competing pathways with similar energy barriers cause the mechanism to be quite complicated. In addition, the short-lived intermediates are difficult to detect, making it challenging to fully characterize the mechanism of these reactions using purely experimental techniques. Therefore, computational chemistry has proven crucial for elucidating the mechanism and shaping our current understanding of these processes. This mechanistic elucidation provides an opportunity to further expand these reactions to new substrates and to refine the selectivity of these reactions.

During the past decade, we have applied computational chemistry, mostly using density functional theory (DFT), to the study of the mechanism of C–C cross-coupling reactions. This Account summarizes the results of our work, as well as significant contributions from others. Apart from a few studies on the general features of the catalytic cycles that have highlighted the existence of manifold competing pathways, most studies have focused on a specific reaction step, leading to the analysis of the oxidative addition, transmetalation, and reductive elimination steps of these processes. In oxidative addition, computational studies have clarified the connection between

coordination number and selectivity. For transmetalation, computation has increased the understanding of different issues for the various named reactions: the role of the base in the Suzuki–Miyaura cross-coupling, the factors distinguishing the cyclic and open mechanisms in the Stille reaction, the identity of the active intermediates in the Negishi cross-coupling, and the different mechanistic alternatives in the Sonogashira reaction. We have also studied the closely related direct arylation process and highlighted the role of an external base as proton abstractor. Finally, we have also rationalized the effect of ligand substitution on the reductive elimination process.
Computational chemistry has improved our understanding of palladium-catalyzed cross-coupling processes, allowing us to identify the mechanistic complexity of these reactions and, in a few selected cases, to fully clarify their mechanisms. Modern computational tools can deal with systems of the size and complexity involved in cross-coupling and have a continuing role in solving specific problems in this field.

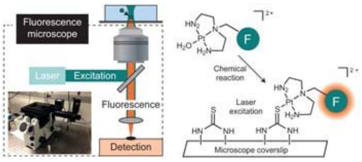
- Interplay of Chemistry and Dynamics in the Low-Mass Star Formation
  Aikawa, Y. *Chem. Rev.* **2013**, *113*, 8961–8980.
  <u>Abstract:</u>



Interstellar space is filled with interstellar gas, which is composed of hydrogen (~71% of mass), He (~27%), and heavier elements (~1%). The gas contains small dust grains of silicate and carbonaceous material, which take up a significant fraction of the heavy elements, ranging from a few to several tens of percent depending on the elements. Density and temperature of the interstellar gas vary spatially. For example, energetic UV radiation from massive stars can ionize hydrogen atoms and heat the gas to ~10^4 K, which is called HII region. In regions relocated from such massive stars, interstellar radiation with <13.6 eV (ionization potential of hydrogen) is still available, and hydrogen is mainly in atomic form. In some regions, interstellar gas is accumulated so that the interstellar radiation is attenuated by dust grains, and the gas becomes molecular. They are called molecular clouds. Due to the radiative cooling and lack of efficient heating source, the typical temperature of molecular clouds is as low as ~10 K. The number density of gas is ~10^3 molecular hydrogen per cubic centimeter (i.e., gas pressure ~10^{-15} Torr) or higher, which is significantly low compared with the gas density in the vacuum chamber in laboratories on Earth but is relatively high in interstellar space.
The evolutionary sequence from molecular clouds to planetary systems described above, and the detection of various molecular lines in each evolutionary stage, naturally give rise to many questions. How are the molecules in molecular clouds and cloud cores incorporated to protoplanetary disks? How is the chemical composition altered during the star- and planet-formation processes? What is the major carrier of volatile elements in disks, and how do they vary as a function of time and distance from the central star? Combinations of hydro-chemical models and observation of star-

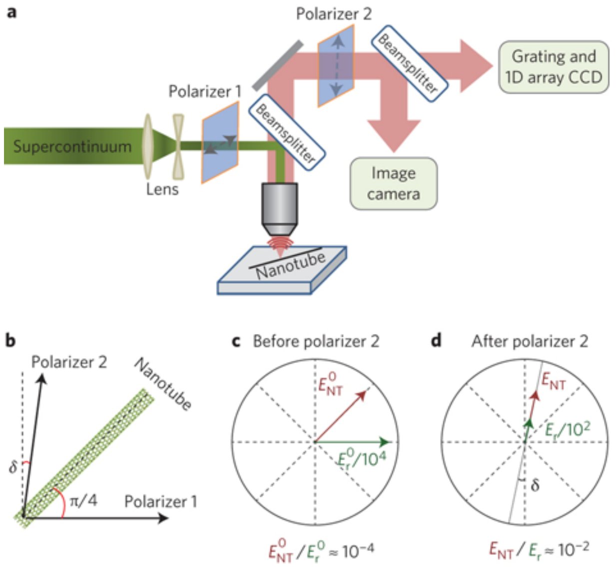
forming cores and disks are powerful tools to tackle these questions. While the chemistry in the disk is reviewed by Henning & Semenov, we will review chemistry in earlier stages, from molecular cloud cores to forming protoplanetary disks. Evolution of water, one of the key molecules for star and planet formation, is reviewed by van Dishoeck et al.

- Opportunities and challenges in single-molecule and single-particle fluorescence microscopy for mechanistic studies of chemical reactions
  Cordes, T.; Blum, S. A. *Nature Chem.* **2013**, *5*, 993–999.
  Abstract:



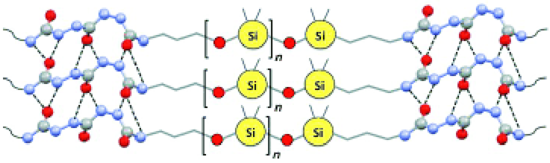
In recent years, single-molecule and single-particle fluorescence microscopy has emerged as a tool to investigate chemical systems. After an initial lag of over a decade with respect to biophysical studies, this powerful imaging technique is now revealing mechanisms of 'classical' organic reactions, spatial distribution of chemical reactivity on surfaces and the phase of active catalysts. The recent advance into commercial imaging systems obviates the need for home-built laser systems and thus opens this technique to traditionally trained synthetic chemists. We discuss the requisite photophysical and chemical properties of fluorescent reporters and highlight the main challenges in applying single-molecule techniques to chemical questions. The goal of this Perspective is to provide a snapshot of an emerging multidisciplinary field and to encourage broader use of this young experimental approach that aids the observation of chemical reactions as depicted in many textbooks: molecule by molecule.

- High-throughput optical imaging and spectroscopy of individual carbon nanotubes in devices
  Liu, K.; Hong, X.; Zhou, Q.; Jin, C.; Li, J.; Zhou, W.; Liu, J.; Wang, E.; Zettl, A.; Wang, F. *Nature Nanotech.* **2013**, *8*, 917–922.
  Abstract:



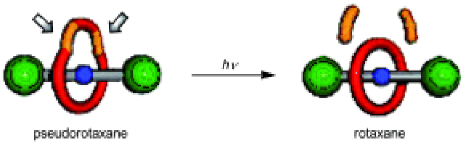
Single-walled carbon nanotubes are uniquely identified by a pair of chirality indices (*n*,*m*), which dictate the physical structures and electronic properties of each species. Carbon nanotube research is currently facing two outstanding challenges: achieving chirality-controlled growth and understanding chirality-dependent device physics. Addressing these challenges requires, respectively, high-throughput determination of the nanotube chirality distribution on growth substrates and *in situ* characterization of the nanotube electronic structure in operating devices. Direct optical imaging and spectroscopy techniques are well suited for both goals, but their implementation at the single nanotube level has remained a challenge due to the small nanotube signal and unavoidable environment background. Here, we report high-throughput real-time optical imaging and broadband *in situ* spectroscopy of individual carbon nanotubes on various substrates and in field-effect transistor devices using polarization-based microscopy combined with supercontinuum laser illumination. Our technique enables the complete chirality profiling of hundreds of individual carbon nanotubes, both semiconducting and metallic, on a growth substrate. In devices, we observe that high-order nanotube optical resonances are dramatically broadened by electrostatic doping, an unexpected behaviour that points to strong interband electron–electron scattering processes that could dominate ultrafast dynamics of excited states in carbon nanotubes.

- The Tris-Urea Motif and Its Incorporation into Polydimethylsiloxane-Based Supramolecular Materials Presenting Self-Healing Features
  Roy, N.; Buhler, E.; Lehn, J.-M. *Chem. Eur. J.* **2013**, *19*, 8814–8820.
  Abstract:



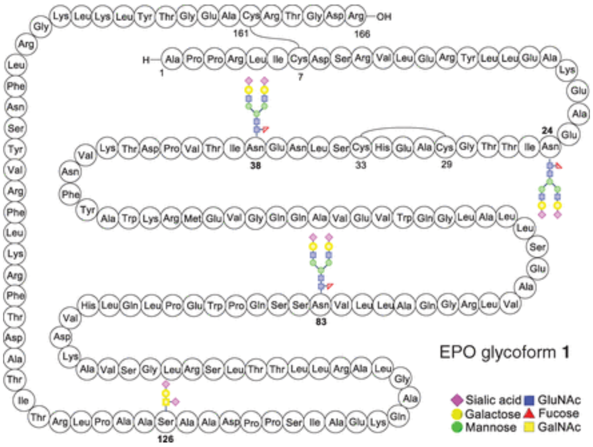
Materials of supramolecular nature have attracted much attention owing to their interesting features, such as self-reparability and material robustness, that are imparted by noncovalent interactions to synthetic materials. Among the various structures and synthetic methodologies that may be considered for this purpose, the introduction of extensive arrays of multiple hydrogen bonds allows for the formation of supramolecular materials that may, in principle, present self-healing behavior. Hydrogen bonded networks implement dynamic noncovalent interactions. Suitable selection of structural units gives access to novel dynamic self-repairing materials by incrementing the number of hydrogen-bonding sites present within a molecular framework. Herein, we describe the formation of a tris-urea based motif giving access to six hydrogen-bonding sites, easily accessible through reaction of carbohydrazide with an isocyanate derivative. Extension towards the synthesis of multiply hydrogen-bonded supramolecular materials has been achieved by polycondensation of carbohydrazide with a bis-isocyanate component derived from poly-dimethylsiloxane chains. Such materials underwent self-repair at a mechanically cut surface. This approach gives access to a broad spectrum of materials of varying flexibility by appropriate selection of the bis-isocyanate component that forms the polymer backbone.

- Using “Threading Followed by Shrinking” to Synthesize Highly Stable Dialkylammonium-Ion-Based Rotaxanes
  Wang, L.-Y.; Ko, J.-L.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Chem. Eur. J.* **2013**, *19*, 8850–8860.
  Abstract:



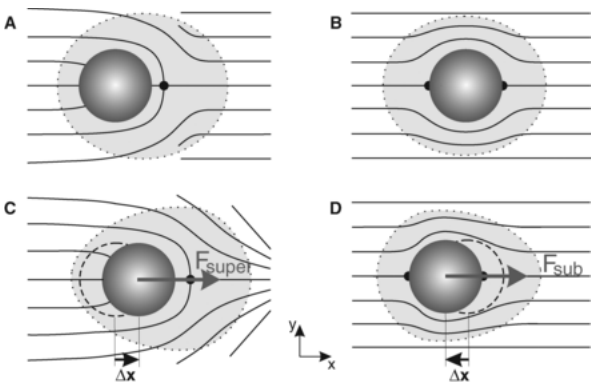
Herein, we report a “threading followed by shrinking” approach for the synthesis of rotaxanes by using an “oxygen-deficient” macrocycle that contained two arylmethyl sulfone units and the dumbbell-shaped salt bis(3,5-dimethylbenzyl)ammonium tetrakis(3,5-trifluoromethylphenyl)borate as the host and guest components, respectively. The extrusion of SO_2 from both of the arylmethyl sulfone units of the macrocyclic component in the corresponding [2]pseudorotaxane resulted in a [2]rotaxane that was sufficiently stable to maintain its molecular integrity in CD_3SOCD_3 at 393 K for at least 5 h.

- Erythropoietin Derived by Chemical Synthesis
  Wang, P.; Dong, S.; Shieh, J.-H.; Peguero, E.; Hendrickson, R.; Moore, M. A. S.; Danishefsky, S. J. *Science* **2013,** *342*, 1357-1360.
  Abstract:



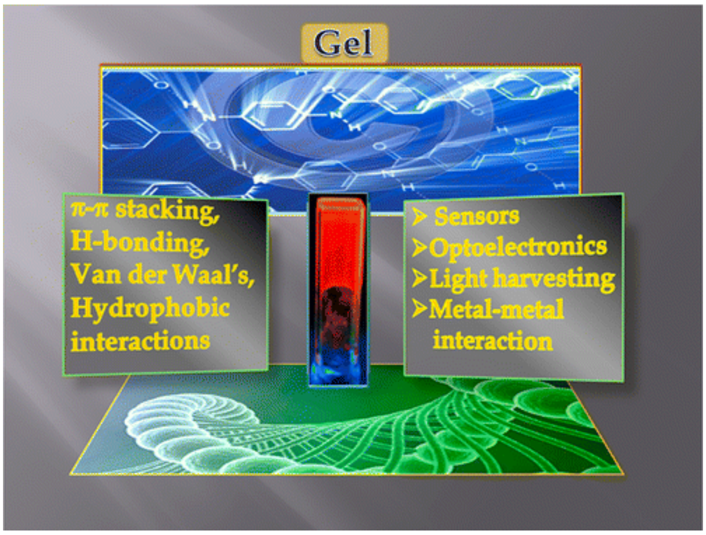
Erythropoietin is a signaling glycoprotein that controls the fundamental process of erythropoiesis, orchestrating the production and maintenance of red blood cells. As administrated clinically, erythropoietin has a polypeptide backbone with complex dishomogeneity in its carbohydrate domains. Here we describe the total synthesis of homogeneous erythropoietin with consensus carbohydrate domains incorporated at all of the native glycosylation sites. The oligosaccharide sectors were built by total synthesis and attached stereospecifically to peptidyl fragments of the wild-type primary sequence, themselves obtained by solid-phase peptide synthesis. The glycopeptidyl constructs were joined by chemical ligation, followed by metal-free dethiylation, and subsequently folded. This homogeneous erythropoietin glycosylated at the three wild-type aspartates with N-linked high-mannose sialic acid–containing oligosaccharides and O-linked glycophorin exhibits Procrit-level in vivo activity in mice.

- Effect of Collective Molecular Reorientations on Brownian Motion of Colloids in Nematic Liquid Crystal
  Turiv, T.; Lazo, I.; Brodin, A.; Lev, B. I.; Reiffenrath, V.; Nazarenko, V. G.; Lavrentovich, O. D. *Science* **2013,** *342*, 1351-1354.
  Abstract:



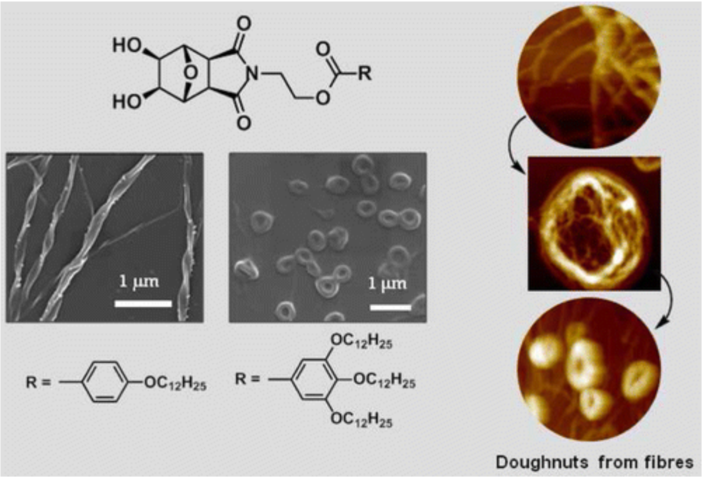
In the simplest realization of Brownian motion, a colloidal sphere moves randomly in an isotropic fluid; its mean squared displacement (MSD) grows linearly with time τ. Brownian motion in an orientationally ordered fluid—a nematic—is anisotropic, with the MSD being larger along the axis of molecular orientation, called the director. We found that at short time scales, the anisotropic diffusion in a nematic becomes anomalous, with the MSD growing slower or faster than τ; these states are respectively termed subdiffusion and superdiffusion. The anomalous diffusion occurs at time scales that correspond to the relaxation times of director deformations around the sphere. Once the nematic melts, the diffusion becomes normal and isotropic. Our experiment shows that the deformations and fluctuations of long-range orientational order profoundly influence diffusive regimes.

- Supramolecular Assemblies of Amide-Derived Organogels Featuring Rigid π-Conjugated Phenylethynyl Frameworks
  Rao, M. R.; Sun, S.-S. *Langmuir* **2013**, *49*, 15146–15158.
  Abstract:



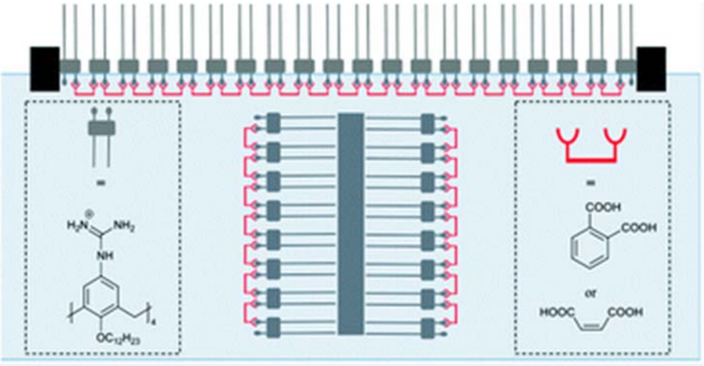
Organogels, being an important class of soft materials, have evolved to be one of the most attractive subjects bridging supramolecular chemistry and material sciences due to their structural diversity and associated physical properties. Myriad applications in fields such as optoelectronics, light harvesting, environmental science, and regenerative medicine are being envisaged. Supramolecular gels usually are formed through self-aggregation of small-molecule gelators to form entangled self-assembled fibrillar networks through a combination of non covalent interactions such as hydrogen bonding, π–π stacking, electrostatic forces, donor–acceptor interactions, metal coordination, solvophobic forces, and van der Waals interactions. This feature article discusses recent and current state of research on amide derived organogelators bearing rigid conjugated phenylethynyl building blocks. Selective examples from our works along with some closely related examples from literature have been highlighted to showcase the structural diversity and their potential applications in supramolecular chemistry and materials science.

- Hierarchical Preferences of Hydroxylated Oxanorbornane-Based Achiral Amphiphiles
  Janni, D. S.; Manheri, M. K. *Langmuir* **2013**, *49*, 15182–15190.
  Abstract:



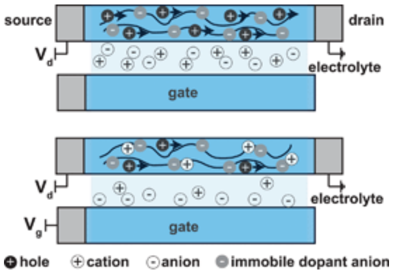
Achiral amphiphiles with hydroxylated oxanorbornane headgroups showed specific morphological characteristics and hierarchical preferences depending upon the nature of lipophilic units. Detailed scanning electron microscopic (SEM) studies showed that twisted ribbonlike aggregates are characteristic of monoalkoxyaryl lipids with hydrocarbon chain length in the range C10–C13; these systems also had a preference toward lamellar arrangement. Asymmetric packing of these lipids is a unique occurrence and shows that the presence of molecular chirality is not an absolute requirement for curvature effects in their supramolecular assemblies. Aryl units in these systems were found to be important for the observed morphological preferences, which became evident from comparative studies involving simple long chain esters without this moiety. Single-crystal X-ray diffraction analysis of one of the lipids from the latter group gave finer details of strong and weak secondary interactions, which operate during their assembly process. Introduction of more than one alkyl chain on the aromatic ring caused a notable shift in the packing propensity toward columnar arrangement. Most of these cone-shaped molecules were found to give doughnut-shaped aggregates from acetone solution through the intermediary of fibrous structures, which was confirmed through SEM, transmission electron microscopic, and atomic force microscopic studies.

- Langmuir-Blodgett monolayer stabilization using supramolecular clips
  Moridi, N.; Wackerlin, C.; Rullaud, V.; Schelldorfer, R.; Jung, T. A.; Shahgaldian, P. *Chem. Commun.* **2013***, 49,* 367-369.
  Abstract:



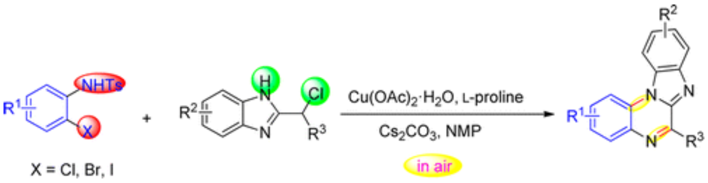
We introduce the concept of stabilization of Langmuir-Blodgett (LB) films using dicarboxylate supramolecular clips, as demonstrated by Langmuir isotherms, spectroscopic ellipsometry, atomic force microscopy, X-ray photoelectron spectroscopy (XPS), and contact angle measurements.

- New opportunities for organic electronics and bioelectronics: ions in action
  Tarabella, G.; Mohammadi, F. M.; Coppede, N.; Barbero, F.; Iannotta, S.; Santato, C.; Cicoira, F. *Chem. Sci.* **2013**, *4,* 1395-1409.
  Abstract:



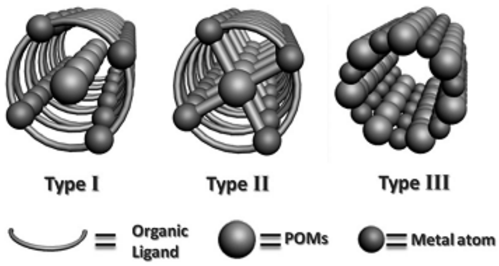
This perspective deals with the coupling of ionic and electronic transport in organic electronic devices, focusing on electrolyte-gated transistors. These include electrolyte-gated organic field-effect transistors (EG-OFETs) and organic electrochemical transistors (OECTs). EG-OFETs, based on molecules and polymers, can be operated at low electrical bias (about 1 V or below) and permit unprecedented charge carrier densities within the transistor channel. OECTs can be operated in aqueous environment as efficient ion-to-electron converters, thus providing an interface between the worlds of biology and electronics. The exploration and the exploitation of coupled ionic and electronic transport in organic materials brings together different disciplines such as materials science, physics, chemistry, electrochemistry, organic electronics and biology.

- An Efficient One-Pot Synthesis of Benzo[4,5]imidazo[1,2-a]quinoxalines via Copper-Catalyzed Process
  Huang, A.; Chen, Y.; Zhou, Y.; Guo, W.; Wu, X.; Ma, C. *Org. Lett.* **2013,** *15*, 5480-5483.
  Abstract:



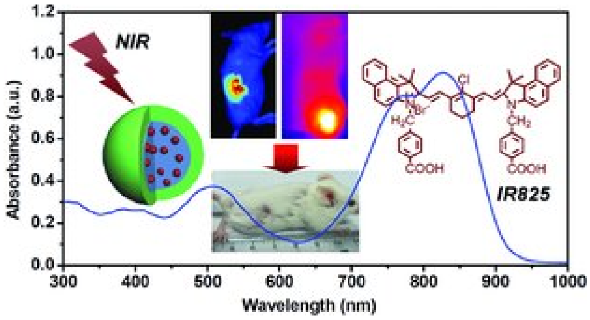
A copper-catalyzed one-pot process for the construction of benzo[4,5]imidazo[1,2-a]quinoxalines under air is described. Aryl chlorides, aryl bromides, and aryl iodides can be applied to the synthesis of these compounds.

- Two Unusual 3D POM-Ag Frameworks with Tetragonal and Dodecagonal Helical Channels
  Sha, J.; Li, M.; Sun, J.; Yan, P.; Li, G.; Zhang, L. *Chem. Asian J.* **2013,** *8*, 2254-2261.
  Abstract:



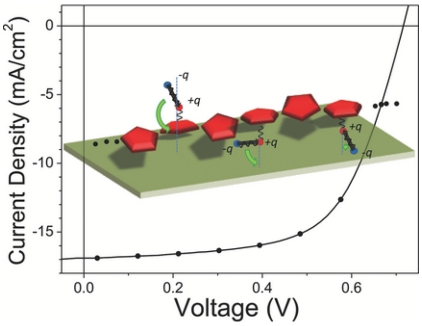
Two new hybrid compounds with tetragonal and dodecagonal helical channels, $K[Ag_{14}(pyttz)_4(H_2O)_2][PW_{12}O_{40}]_2\cdot(OH)\cdot5H_2O$**(1)** and $K[Ag_{14}(pyttz)_4(H_2O)_4][HSiW_{12}O_{40}]_2\cdot H_2O$**(2)**, have been hydrothermally synthesized and structurally characterized by using routine techniques. X-ray diffraction analysis shows that compounds **1** and **2** are isostructural and crystallize in themonoclinic space group $P2_1/c$. A fascinating structural feature of these compounds is that they form 3D POM-Ag frameworks with helical channels, which are the first examples of helical channels that are constructed from POMs and metal atoms. Notably, there are two types of spatial orientation of the POMs, which result in the formations of left- and right-handed helical chains. Furthermore, these different helical chains are perfectly enclosed through shared POMs, thereby forming tetragonal and dodecagonal helical channels. In addition, the photocatalytic degradation of RhB by these compounds was also investigated.

- PEGylated Micelle Nanoparticles Encapsulating a Non-Fluorescent Near-Infrared Organic Dye as a Safe and Highly-Effective Photothermal Agent for In Vivo Cancer Therapy
  Cheng, L.; He, W.; Gong, H.; Wang, C.; Chen, Q.; Cheng, Z.; Liu, Z. *Adv.Funct. Mater*. **2013**, *23*, 5893-5902.
  Abstract:



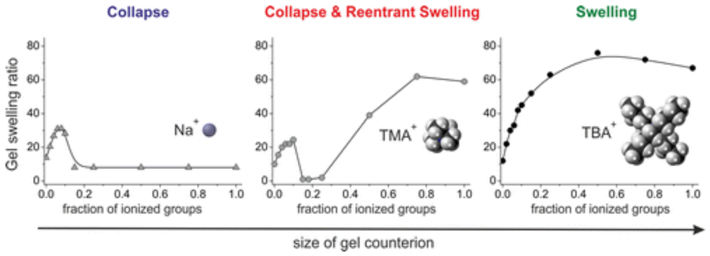
Photothermal therapy (PTT), as a minimally invasive and highly effective cancer treatment approach, has received widespread attention in recent years. Tremendous effort has been devoted to explore various types of photothermal agents with high near-infrared (NIR) absorbance for PTT cancer treatment. Despite many exciting progresses in the area, effective yet safe photothermal agents with good biocompatibility and biodegradability are still highly desired. In this work, a new organic PTT agent based on polyethylene glycol (PEG) coated micelle nanoparticles encapsulating a heptamethine indocyanine dye IR825 is developed, showing a strong NIR absorption band and a rather low quantum yield, for in vivo photothermal treatment of cancer. It is found that the IR825–PEG nanoparticles show ultra-high in vivo tumor uptake after intravenous injection, and appear to be an excellent PTT agent for tumor ablation under a low-power laser irradiation, without rendering any appreciable toxicity to the treated animals. Compared with inorganic nanomaterials and conjugated polymers being explored in PTT, the NIR-absorbing micelle nanoparticles presented here may have the least safety concern while showing excellent treatment efficacy, and thus may be a new photothermal agent potentially useful in clinical applications.

- Conjugated Polymeric Zwitterions as Efficient Interlayers in Organic Solar Cells
  Liu, F.; Page, Z. A.; Duzhko, V. V.; Russell, T. P.; Emrick, T. *Adv. Funct. Mater*. **2013**, *25*, 6868-6873.
  Abstract:



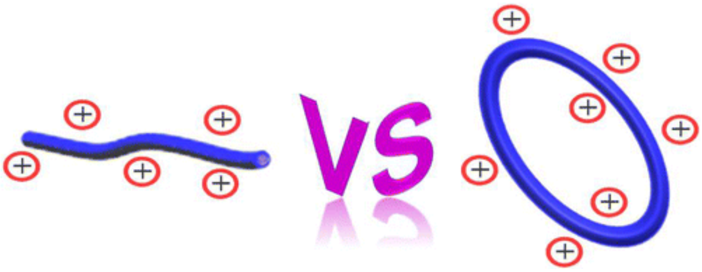
Conjugated polymeric zwitterions, when utilized as interlayer materials in bulk heterojunction organic solar cells, lead to significantly enhanced power conversion efficiencies. The electrostatic model of self-aligning dipolar side groups in the vicinity of the metal surface rationalizes the effects of reduced cathode work function, a key factor behind the observed enhanced efficiency.

- New Type of Swelling Behavior upon Gel Ionization: Theory vs Experiment
  Philippova, O. E.; Rumyantsev, A. M.; Kramarenko, E. Y.; Khokhlov, A. R. *Macromolecules* **2013**, *46*, 9359–9367.
  Abstract:



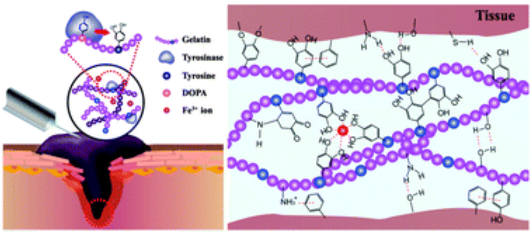
We report a combined experimental and theoretical study on the swelling behavior of polyelectrolyte gels with various types of counterions. Experimental research was focused on poly(methacrylic acid) and poly(acrylic acid) gels in methanol neutralized with different bases providing sodium, cesium, tetramethyl-, tetraethyl- or tetrabutylammonium counterions. The novelty of the theoretical treatment is that the counterion size is explicitly taken into account as well as the dependence of the ion association constant on the volume fraction of polymer within the gel. We demonstrate that, depending on the counterion size, three different regimes of the gel behavior are realized. In case of bulky tetrabutylammonium counterions the gel swells upon ionization. For small counterions (Na^+, Cs^+) the gel swelling at low ionization degrees is succeeded by its collapse. New type of behavior was observed and theoretically described for the gels with counterions of intermediate sizes (tetramethyl- and tetraethylammonium). In this case, the gel ionization causes first swelling, then collapse and finally reswelling of the gel. This distinction in gel behavior with counterions of different types is explained by decreasing tendency for ion pair and multiplet formation with growing counterion dimensions. Our finding of the counterion-controlled collapse/decollapse transition is significant for fundamental understanding of the role of ion association processes in polyelectrolyte gel behavior as well as for design of sensors and environmentally responsive containers for controlled delivery applications.

- Synthesis and Evaluation of Cyclic Cationic Polymers for Nucleic Acid Delivery
  Wei, H.; Chu, D. S. H.; Zhao, J.; Pahang, J. A.; Pun, S. H. *ACS Macro Lett.* **2013**, *2*, 1047–1050.
  Abstract:



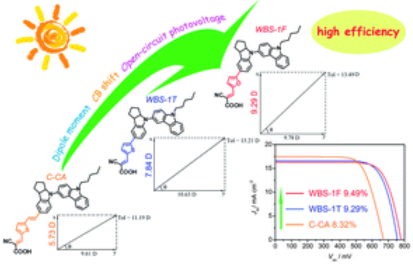
The architecture of polycation gene carriers has been shown to affect both their transfection efficiency and cytotoxicity. This work reports the synthesis of cyclic polycations and their use for gene transfer to mammalian cells. Cyclic poly((2-dimethylamino) ethylmethacrylate) (pDMAEMA) homopolymers of various molecular weights were synthesized by “intrachain”click cyclization of α-alkyne-ω-azide heterodifunctional linear precursors prepared by atom transfer radical polymerization (ATRP). Polymers were characterized by size exclusion chromatography and FT-IR analyses to confirm efficient cyclization and products with low polydispersity. Cyclic polymers formed more compact particles with plasmid DNA compared to linear analogues. Cellular uptake, membrane disruption, and nucleic acid delivery efficiency were determined for all polymers. In general, cyclic polymers complexed and delivered nucleic acids with efficiencies similar to their linear counterparts. Notably, cyclic polymers were less cytotoxic than linear polymers due to reduced membrane disruption and are therefore promising alternative structures for biological applications.

- Human gelatin tissue-adhesive hydrogels prepared by enzyme-mediated biosynthesis of DOPA and Fe^{3+} ion crosslinking
  Choi, Y. C.; Choi, J. S.; Junga, Y. J.; Cho, Y. W. *J. Mater. Chem. B,* **2014**, *2*, 201–209.
  Abstract:



Gelatin is extensively used as a biomaterial for diverse pharmaceutical and medical applications due to its excellent biocompatibility and biodegradability. Here we present bio-inspired tissue-adhesive gelatin hydrogels prepared by the enzyme-mediated synthesis of L-3,4-dihydroxyphenylalanine (L-DOPA) and Fe^{3+} ion crosslinking. Gelatin of human origin was obtained through two major steps, extracellular matrix (ECM) extraction from human adipose tissue and gelatin isolation from the ECM. The tyrosine residues in human gelatin were converted into DOPA by enzymatic reaction with tyrosinase. Upon the addition of Fe^{3+} ions, the DOPA-modified gelatin formed a sticky hydrogel within seconds through complexation between the DOPA molecules and Fe^{3+} ions. The final DOPA-modified, Fe^{3+} ion-crosslinked gelatin hydrogels retained their hydrogel stability well at body temperature in an aqueous environment and exhibited appropriate mechanical properties. The hemostatic ability of the DOPA–Fe^{3+} gelatin hydrogels was explored using a hemorrhaging liver rat model. Shortly after the injection of the DOPA–Fe^{3+} gelatin hydrogel, the bleeding was arrested in the hemorrhaging site of the liver. Overall results suggest that the DOPA–Fe^{3+} gelatin hydrogel, with its good elastic and hemostatic properties, is a promising tissue adhesive for use in a wide variety of surgical operations.

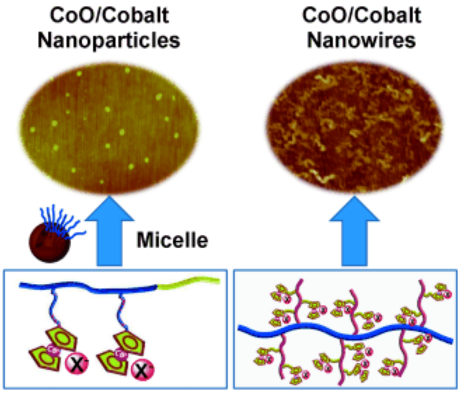
- Influence of conjugated π-linker in D–D–π–A indoline dyes: towards long-term stable and efficient dye-sensitized solar cells with high photovoltage
  Liu, B.; Wang, B.; Wang, R.; Gao, L.; Huo, S.; Liu, Q.; Lia, X.; Zhu, W. *J. Mater. Chem. A,* **2014**, *2,* 804–812.
  Abstract:



The judicious choice of conjugated π-linkers is a critical strategy towards the energy-level engineering of donor–π–acceptor (D–π–A) sensitizers. Given that the vinyl bond on π-bridge thiophene segment can deteriorate its intrinsic photo-stability, we systematically study three D–D–π–A indoline dyes **C-CA**, **WBS-1T** and **WBS-1F** with different conjugated π-linkers (vinylthiophene, thiophene and furan) for high efficiency, long-term stable dye-sensitized solar cells (DSSCs). Compared with the vinylthiophene unit in **C-CA**, the conjugated π-linker of the thiophene or furan group in **WBS-1T** and **WBS-1F** can improve the solar cell performance with a great enhancement in the open-circuit photovoltage (V_{OC}). As an overall result of the upshift of the TiO_2 conduction band (CB) edge and the slow charge recombination, the V_{OC} values are in the order **WBS-1F** (779 mV) > **WBS-1T** (756 mV) > **C-CA** (670 mV). Moreover, the CB edge shift of TiO_2 is the major contribution to the large difference in V_{OC}, accounting for 80% of the enhancement. Both the stepped light-induced transient measurements (SLIT) and the molecular dipole simulation are accounted for well by the observed superior photovoltage upon removal of the vinyl group in the conjugated π-linker. The higher molecular dipole moments can bring forth a more effective charge separation between donor and acceptor units, resulting in a remarkable increase in V_{OC}. Using a liquid electrolyte, **WBS-1F** shows an impressively high efficiency of 9.49% with a high photovoltage of 779 mV. Its efficiency reaches 8.03% with ionic-liquid electrolyte while it reduces to 7.60% after a 1000 h aging test. Our work has shown that for D–π–A organic dyes, the vinyl unit in the conjugated π-linker is detrimental to the molecular dipole moment, the upshift of TiO_2 CB edge, and the suppression of charge recombination, as well as the photo-stability.

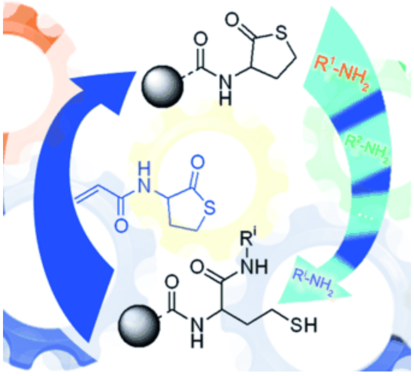
- Charged Metallopolymers as Universal Precursors for Versatile Cobalt Materials
  Zhang, J.; Yan, Y.; Chance, M. W.; Chen, J.; Hayat, J.; Ma, S.; Tang, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 13387–13391.

Abstract:



A facile phase-transfer ion-exchange strategy was used to prepare cationic cobaltocenium-containing polyelectrolytes with different counterions. These cobalt-containing polymers were used to prepare cobalt-based materials, including cobalt metal, cobalt phosphide, cobalt monoxide, cobalt–iron hybrids, and cobalt ferrite. Block copolymers and polymer brushes were also used to prepare cobalt-based nanoparticles and nanowires.

- Multifunctionalized Sequence-Defined Oligomers from a Single Building Block
  Espeel, P.; Carrette, L. L. G.; Bury, K.; Capenberghs, S.; Martins, J. C.; Du Prez, F. E.; Madder, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 13261–13264.
  Abstract:



Another link in the chain: A thiolactone-based approach for the preparation of multifunctionalized sequence-defined oligomeric structures on solid support was established. The iterative aminolysis/chain extension method with a single building block and a variety of commercial amines allowed for the protecting group free synthesis of various oligomeric motifs with a unique backbone and a preprogrammed organization of side chain functionalities.