• Side-chain control of porosity closure in single- and multiple-peptide-based porous materials by cooperative folding
Abstract:

Porous materials are attractive for separation and catalysis—these applications rely on selective interactions between host materials and guests. In metal-organic frameworks (MOFs), these interactions can be controlled through a flexible structural response to the presence of guests. Here we report a MOF that consists of glycy1-serine dipeptides coordinated to metal centres, and has a structure that evolves from a solvated porous state to a desolvated non-porous state as a result of ordered cooperative, displacive and conformational changes of the peptide. This behaviour is driven by hydrogen bonding that involves the side-chain hydroxyl groups of the serine. A similar cooperative closure (reminiscent of the folding of proteins) is also displayed with multipeptide solid solutions. For these, the combination of different sequences of amino acids controls the framework’s response to the presence of guests in a nonlinear way. This functional control can be compared to the effect of single-point mutations in proteins, in which exchange of single amino acids can radically alter structure and function.

• Expanding ester biosynthesis in Escherichia coli
Abstract:

To expand the capabilities of whole-cell biocatalysis, we have engineered Escherichia coli to produce various esters. The alcohol O-acyltransferase (ATF) class of enzyme uses acyl-CoA units for ester formation. The release of free CoA upon esterification with an alcohol provides the free energy to facilitate ester formation. The diversity of CoA molecules found in nature in combination with various alcohol biosynthetic pathways allows for the biosynthesis of a multitude of esters. Small to medium volatile esters have extensive applications in the flavor, fragrance, cosmetic, solvent, paint and coating industries. The present work enables the production of these compounds by designing
several ester pathways in *E. coli*. The engineered pathways generated acetate esters of ethyl, propyl, isobutyl, 2-methyl-1-butyl, 3-methyl-1-butyl and 2-phenylethyl alcohols. In particular, we achieved high-level production of isobutyl acetate from glucose (17.2 g l⁻¹). This strategy was expanded to realize pathways for tetradecyl acetate and several isobutyrate esters.

- **Dendrimer–surfactant interactions**  
  **Abstract:**

  In this article, we reviewed the interactions between dendrimers and surfactants with particular focus on the interaction mechanisms and physicochemical properties of the yielding dendrimer–surfactant aggregates. In order to provide insight into the behavior of dendrimers in biological systems, the interactions of dendrimers with bio-surfactants such as phospholipids in bulk solutions, in solid-supported bilayers and at the interface of phases or solid-states were discussed. Applications of the dendrimer–surfactant aggregates as templates to guide the synthesis of nanoparticles and in drug or gene delivery were also mentioned.

- **Interfacial assembly of ZnO quantum dots into giant supramolecular architectures**  
  **Abstract:**

  Para-aminobenzoic acid (PABA) stabilised zinc oxide (ZnO) quantum dots (QDs) have been synthesised by refluxing zinc acetate dihydrate in methanol under alkaline condition and re-dispersed into water by centrifugation. Aqueous dispersion of PABA-stabilised ZnO QDs was taken with seven different organic solvents in test tubes and subjected to diazo reaction under specified conditions. It was seen that the quantum dots assembled into diverse superstructures depending on the nature of the immiscible solvent at the aqueous–organic interface. The assemblies so obtained have been characterised by energy dispersive X-ray (EDX) analysis, Fourier transform infrared (FTIR), fluorescence and Raman spectroscopy, X-ray diffraction (XRD) and thermogravimetric analysis (TGA), optical, fluorescence and scanning electron microscopic (SEM) images. It has been observed that the ensuing supramolecular assemblies exhibit significant electrical conductivity and photoluminescence properties.
• Synthesis of Doubly Ethyl-Bridged Bis(p-sulfonatocalix[4]arene) and Its Supramolecular Polymerization with Viologen Dimer


Abstract:

A water-soluble supramolecular polymer with a high degree of polymerization and viscosity has been constructed based on the strong host–guest interaction between p-sulfonatocalix[4]arenes (SC4As) and viologen. A homoditopic doubly ethyl-bridged bis(p-sulfonatocalix[4]arene) (d-SC4A) was prepared and its binding behavior towards methyl viologen compared with the singly ethyl-bridged bis(p-sulfonatocalix[4]arene) (s-SC4A) by NMR spectroscopy and isothermal titration calorimetry. By employing a viologen dimer (bisMV4+) as the homoditopic guest, two linear AA/BB-type supramolecular polymers, d-SC4A~bisMV4+ and s-SC4A~bisMV4+, were successfully constructed. Compared with s-SC4A~bisMV4+, d-SC4A~bisMV4+ shows much higher solubility and viscosity, and has also been characterized by viscosity, diffusion-ordered NMR spectroscopy, dynamic light scattering, and atomic force microscopy measurements. Furthermore, the polymer is responsive to electrostimulus as viologen is electroactive, which was studied by cyclic voltammetry. This study represents a proof-of-principle as the polymer can potentially be applied as a self-healing and degradable polymeric material.

• Solvent-Dependent Self-Assembly Behaviour and Speciation Control of Pd₆L₈ Metallo-supramolecular Cages.


Abstract:

The C₃-symmetric chiral propylated host-type ligands (±)-tris(isonicotinoyl)-tris(propyl)-cyclooctatetraene (L1) and (±)-tris(4-pyridyl-4-benzoxy)-tris(propyl)-cyclooctatetraene (L2) self-assemble with Pd¹⁺ into [Pd₆L₈]¹²⁺ metallo-cages that resemble a stella octangula. The self-assembly of the [Pd₆(L1)]¹²⁺ cage is solvent-dependent; broad NMR resonances and a disordered crystal structure indicate no chiral self-sorting of the ligand enantiomers in DMSO solution, but sharp NMR resonances occur in MeCN or MeNO₂. The [Pd₆(L1)]¹²⁺ cage is observed to be less favourable in the
presence of additional ligand, than is its counterpart, where \( L=(\pm)\text{-tris(isonicotinoyl)cyclotriguaiacylene (L1a)} \). The stoichiometry of reactant mixtures and chemical triggers can be used to control formation of mixtures of homoleptic or heteroleptic \([\text{Pd}_6\text{L}_8]^{12+}\) metallo-cages where \( L=L1 \) and \( L1a \).

- DNA-templated nanowires: morphology and electrical conductivity
  **Abstract**

  DNA-templating has been used to create nanowires from metals, compound semiconductors and conductive polymers. The mechanism of growth involves nucleation at binding sites on the DNA followed by growth of spherical particles and then, under favourable conditions, a slow transformation to a smooth nanowire. The final transformation is favoured by restricting the amount of templated material per unit length of template and occurs most readily for materials of low surface tension. Electrical measurements on DNA-templated nanowires can be facilitated using three techniques: (i) standard current–voltage measurements with contact electrodes embedded in a dielectric so that there is a minimal step height at the dielectric/electrode boundary across which nanowires may be aligned by molecular combing, (ii) the use of a dried droplet technique and conductive AFM to determine contact resistance by moving the tip along the length of an individual nanowire and (iii) non-contact assessment of conductivity by scanned conductance microscopy on Si/SiO\(_2\) substrates.

- Electrophoretic self-assembly of expanded mesocarbon microbeads with attached nickel nanoparticles as a high-rate electrode for supercapacitors
  **Abstract:**

  Expanded mesocarbon microbeads (EMCMBs) with graphene oxide (GO) sheets were prepared by expanding graphitized mesocarbon microbeads (MCMBs) using a simple solution-based oxidative process. EMCMB-supported nickel nanoparticles with an average size of 4.6 nm were fabricated by an electrophoretic deposition (EPD) method in the presence of nickel nitrate additive. Nickel ions
were self-assembled on the fluffy GO sheets resulting in a more positively charged EMCMB particle for facilitating EPD and dispersion. After heat treatment at 300 °C, GO could be converted to graphene which could provide a conductive network for facilitating the transport of electrons. Well-dispersed nickel nanoparticles on graphene sheets could act as a redox center to allow storage of extra charge and a nanospacer to prevent the graphene sheets from restacking. The specific capacitance of EMCMB-supported nickel electrode could reach 491 F g⁻¹, which is much higher than that of EMCMB electrode (43 F g⁻¹) and bare nickel electrode (146 F g⁻¹) at a discharge current of 5 A g⁻¹. More importantly, the EMCMB-supported nickel electrode is capable of delivering a high specific capacitance of 440 F g⁻¹ at a discharge current of 50 A g⁻¹, and could pave the way towards high-rate supercapacitors.

- Dramatically Increased pH and Temperature Stability of Chymotrypsin Using Dual Block Polymer-Based Protein Engineering
  Abstract:

  ![Diagram](image)

  In this study, we report on multimodal temperature-responsive chymotrypsin-poly(sulfobetaine methacrylamide)-block-poly(N-isopropylacrylamide) (CT-pSBAm-block-pNIPAm) protein–polymer conjugates. Using polymer-based protein engineering (PBPE) with aqueous atom transfer radical polymerization (ATRP), we synthesized three different molecular weight CT-pSBAm-block-pNIPAm bioconjugates that responded structurally to both low and high temperature. In the block copolymer grown from the surface of the enzyme, upper critical solution temperature (UCST) phase transition was dependent on the chain length of the polymers in the conjugates, whereas lower critical solution temperature (LCST) phase transition was independent of molecular weight. Each CT-pSBAm-block-pNIPAm conjugate showed temperature dependent changes in substrate affinity and productivity when assayed from 0 to 40 °C. In addition, these conjugates showed higher stability to harsh conditions, including temperature, low pH, and protease degradation. Indeed, the PBPE-modified enzyme was active for over 8 h in the presence of a stomach protease at pH 1.0. Using PBPE, we created a dual zone shell surrounding each molecule of enzyme. The thickness of each zone of the shell was engineered to be separately responsive to temperature.

- Tuning Gelation Time and Morphology of Injectable Hydrogels Using Ketone–Hydrazide Cross-Linking
  Abstract:
Injectable, covalently in situ forming hydrogels based on poly(N-isopropylacrylamide) have been designed on the basis of mixing hydrazide-functionalized nucleophilic precursor polymers with electrophilic precursor polymers functionalized with a combination of ketone (slow reacting) and aldehyde (fast reacting) functional groups. By tuning the ratio of aldehyde:ketone functional groups as well as the total number of ketone groups in the electrophilic precursor polymer, largely independent control over hydrogel properties including gelation time (from seconds to hours), degradation kinetics (from hours to months), optical transmission (from 1 to 85%), and mechanics (over nearly 1 order of magnitude) can be achieved. In addition, ketone-functionalized precursor polymers exhibit improved cytocompatibility at even extremely high concentrations relative to polymers functionalized with aldehyde groups, even at 4-fold higher functional group densities. Overall, increasing the ketone content of the precursor copolymers can result in in situ-gellable hydrogels with improved transparency and biocompatibility and equivalent mechanics and stimuli-responsiveness while only modestly sacrificing the speed of gel formation.

- Heterocyclization of Enediyynes Promoted by Sodium Azide: A Case of Ambiguity of X-ray Data and Structure Revision
  Abstract:

  ![Reaction Scheme]

  It has been shown that contrary to the literature data the tandem cyclization of (Z)-1-aryl-3-hexen-1,5-diyynes promoted by sodium azide results in the formation of the corresponding [1,2,3]triazolo[1,5-a]pyridines, not 1H-benzotriazole derivatives. Apparently, incorrect structure elucidation made by previous investigators originates from misinterpretation of X-ray data. A number of new transformations of this type as well as X-ray and NMR experiments are discussed.

- Chemiluminescence Sensing of Fluoride Ions Using a Self-Immolative Amplifier
  Abstract:
An enhanced chemiluminescence signal is obtained when electronically triggered dioxetane cleavage is initiated by fluoride-mediated deprotection of the silyl-protecting group, followed by self-immolation via 1,4-quinone–methide rearrangement. The reaction takes place even when the probe is trapped within a PMMA layer on top of a glass plate. In that arrangement, fluoride in aqueous solutions can be detected selectively at low micromolar concentrations.

- **Mutual Induced Fit in a Synthetic Host-Guest System**
  **Abstract:**

Mutual induced fit is an important phenomenon in biological molecular recognition, but it is still rare in artificial systems. Here we report an artificial host-guest system in which a flexible calix[4]arene is enclathrated in a dynamic self-assembled host and both molecules mutually adopt specific three-dimensional structures. NMR data revealed the conformational changes, and crystallographic studies clearly established the precise structures at each stage.

- **Reversible Near-Infrared Light Directed Reflection in a Self-Organized Helical Superstructure Loaded with Upconversion Nanoparticles**
  **Abstract:**
Adding external, dynamic control to self-organized superstructures with desired functionalities is an important leap necessary in leveraging the fascinating molecular systems for applications. Here, the new light-driven chiral molecular switch and upconversion nanoparticles, doped in a liquid crystal media, were able to self-organize into an optically tunable helical superstructure. The resulting nanoparticle impregnated helical superstructure was found to exhibit unprecedented reversible near-infrared (NIR) light-guided tunable behavior only by modulating the excitation power density of a continuous-wave NIR laser (980 nm). Upon irradiation by the NIR laser at the high power density, the reflection wavelength of the photonic superstructure red-shifted, whereas its reverse process occurred upon irradiation by the same laser but with the lower power density. Furthermore, reversible dynamic NIR-light-driven red, green, and blue reflections in a single thin film, achieved only by varying the power density of the NIR light, were for the first time demonstrated.

- Responsive Supramolecular Polymer Metallogel Constructed by Orthogonal Coordination-Driven Self-Assembly and Host/Guest Interactions
  Abstract:
  
  An emerging strategy for the fabrication of advanced supramolecular materials is the use of hierarchical self-assembly techniques wherein multiple orthogonal interactions between molecular precursors can produce new species with attractive properties. Herein, we unify the spontaneous formation of metal–ligand bonds with the host/guest chemistry of crown ethers to deliver a 3D supramolecular polymer network (SPN). Specifically, we have prepared a highly directional dipyridyl donor decorated with a benzo-21-crown-7 moiety that undergoes coordination-driven self-assembly with a complementary organoplatinum acceptor to furnish hexagonal metallacycles. These hexagons subsequently polymerize into a supramolecular network upon the addition of a bisammonium salt due to the formation of [2]pseudorotaxane linkages between the crown ether and ammonium moieties. At high concentrations, the resulting 3D SPN becomes a gel comprising many cross-linked metallohexagons. Notably, thermo- and cation-induced gel–sol transitions are found to be completely reversible, reflecting the dynamic and tunable nature of such supramolecular materials. As such, these results demonstrate the structural complexity that can be obtained when carefully controlling multiple interactions in a hierarchical fashion, in this case coordination and host/guest chemistry, and the interesting dynamic properties associated with the materials thus obtained.
Small Molecule Regulation of Self-Association and Catalytic Activity in a Supramolecular Coordination Complex

Abstract:
Herein, we report the synthesis and characterization of the first weak-link approach (WLA) supramolecular construct that employs the small molecule regulation of intermolecular hydrogen bonding interactions for the in situ control of catalytic activity. A biaryl urea group, prone to self-aggregation, was functionalized with a phosphinoalkyl thioether (P,S) hemilabile moiety and incorporated into a homoligated Pt(II) tweezer WLA complex. This urea-containing construct, which has been characterized by a single crystal X-ray diffraction study, can be switched in situ from a rigid fully closed state to a flexible semiopen state via Cl– induced changes in the coordination mode at the Pt(II) structural node. FT-IR and 1H NMR spectroscopy studies were used to demonstrate that while extensive urea self-association persists in the flexible semiopen complex, these interactions are deterred in the rigid, fully closed complex because of geometric and steric restraints. Consequently, the urea moieties in the fully closed complex are able to catalyze a Diels-Alder reaction between cyclopentadiene and methyl vinyl ketone to generate 2-acetyl-5-norbornene. The free urea ligand and the semiopen complex show no such activity. The successful incorporation and regulation of a hydrogen bond donating catalyst in a WLA construct open the doors to a vast and rapidly growing catalogue of allosteric catalysts for applications in the detection and amplification of organic analytes.

Electropolymerization of Polypyrrole by Bipolar Electrochemistry in an Ionic Liquid

Abstract:
Bipolar electrochemistry has been recently explored for the modification of conducting micro- and nanoobjects with various surface layers. So far, it has been assumed that such processes should be carried out in low-conductivity electrolytes in order to be efficient. We report here the first bipolar electrochemistry experiment carried out in an ionic liquid, which by definition shows a relatively high conductivity. Pyrrole has been electropolymerized on a bipolar electrode, either in ionic liquid or in acetonitrile. The resulting polymer films were characterized by scanning electron microscopy and by contact profilometry. We demonstrate that the films obtained in an ionic liquid are thinner and smoother than the films synthesized in acetonitrile. Furthermore, a well-defined band of polypyrrole can be obtained in ionic liquid, in contrast to acetonitrile for which the polypyrrole film is present on the whole anodic part of the bipolar electrode.

- Amyloid β Peptide Conformational Changes in the Presence of a Lipid Membrane System
  Abstract:

Here we are presenting a comparative analysis of conformational changes of two amyloid β peptides, Aβ(25–35) and Aβ(1–42), in the presence and absence of a phospholipid system, namely, POPC/POPS (1-palmitoyl-2-oleoylphosphatidylcholine/palmitoyl-2-oleoylphosphatidylserine), through Raman spectroscopy, synchrotron radiation micro Fourier-transform infrared spectroscopy, and micro X-ray diffraction. Ringlike samples were obtained from the evaporation of pure and mixed solutions of the proteins together with the POPC/POPS system on highly hydrophilic substrates. The results confirm the presence of a α-helical to β-sheet transition from the internal rim of the ringlike samples to the
external one in the pure Aβ(25–35) residual, probably due to the convective flow inside the droplets sitting on highly hydrophilic substrates enhancing the local concentration of the peptide at the external edge of the dried drop. In contrast, the presence of POPC/POPS lipids in the peptide does not result in α-helical structures and introduces the presence of antiparallel β-sheet material together with parallel β-sheet structures and possible β-turns. As a control, Aβ(1–42) peptide was also tested and shows β-sheet conformations independently from the presence of the lipid system. The μXRD analysis further confirmed these conclusions, showing how the absence of the phospholipid system induces in the Aβ(25–35) a probable composite α/β material while its coexistence with the peptide leads to a not oriented β-sheet conformation. These results open interesting scenarios on the study of conformational changes of Aβ peptides and could help, with further investigations, to better clarify the role of enzymes and alternative lipid systems involved in the amyloidosis process of Aβ fragments.

• Best of Both Worlds: Conjugated Polymers Exhibiting Good Photovoltaic Behavior and High Tensile Elasticity

Abstract:

This paper examines a series of poly(3-alkylthiophene)s (P3ATs), a class of materials for which mechanical compliance and electronic performance have been observed to be in competition. P3ATs with longer alkyl side chains (n ≥ 8) have high elasticity and ductility, but poor electronic performance (as manifested in photovoltaic efficiency in blends with fullerenes); P3ATs with shorter chains (n ≤ 6) exhibit the opposite characteristics. A series of four polymer films in which the average length of the side chain is n = 7 is tested using mechanical, spectroscopic, microscopic, and photovoltaic device-based measurements to determine whether or not it is possible, in principle, to maximize both mechanical and electronic performance in a single organic semiconductor (the “best of both worlds”). The four polymer samples are (1) a physical blend of equal parts P3HT and P3OT (P3HT:P3OT, n = 6 and n = 8), (2) a block copolymer (P3HT-b-P3OT), (3) a random copolymer (P3HT-co-P3OT), and (4) poly(3-heptylthiophene) (P3HpT, n = 7). The tensile moduli obtained by mechanical buckling correlate well with spectroscopic evidence (using the weakly interacting H aggregate model) of a well-ordered microstructure of the polymers. The block copolymer was the stiffest of the hybrid samples (680 ± 180 MPa), while P3HpT exhibited maximum compliance (70 ± 10 MPa) and power conversion efficiency in a 1:1 blend with the fullerene PC61BM using stretchable electrodes (PCE = 2.16 ± 0.17%) that was similar to that of P3HT:PC61BM. These analyses may permit the design of organic semiconductors with improved mechanical and electronic properties for mechanically robust and stretchable applications.
Nanostructure and Rheology of Hydrogen-Bonding Telechelic Polymers in the Melt: From Micellar Liquids and Solids to Supramolecular Gels

Abstract:

Polymers with hydrogen-bonding groups in the melt state often combine the ability to form specific supramolecular bonds with a tendency for unspecific aggregation and microphase separation. Using a combination of small-angle X-ray scattering and shear spectroscopy, we present a study of structure formation and rheological properties of such a case, an exemplary series of telechelic polyisobutylene, functionalized with hydrogen-bonding end groups. Unspecific interaction between hydrogen-bonding groups leads to the formation of micelles. For monofunctional samples, we observe ordering at lower temperatures, induced by a temperature dependent concentration of the micelles. The rheological properties of these systems can be mapped to the behavior of a concentrated colloidal fluid or solid. For bifunctional polymers with complementary hydrogen-bonding groups, interaction between micellar aggregates leads to network formation and solidlike properties at lower temperatures induced by gelation without ordering. Only in this case the supramolecular bonds directly determine the rheological properties.

Towards an understanding of structure-nonlinearity relationships in triarylamine-based push-pull electro-optic chromophores: the influence of substituent and molecular conformation on molecular hyperpolarizabilities

Abstract:

We calculated the second-order hyperpolarizability (β) of a series of triarylamine (TAA) based donor–bridge–acceptor (D–π–A) push–pull type nonlinear optical (NLO) chromophores with different electron donor moieties and the same thiophene π-bridge and dicyanovinyl electron acceptor using a time-dependent Hartree–Fock (TDHF) approach within the software package MOPAC 2012. NLO chromophores with various quantities and positions of methoxy groups in the TAA donor moiety were investigated. The relationship between NLO properties and the electronic or geometric structures of the TAA donor subunit is discussed through the calculation results. Both substituent and
conformational effects affect the delocalization of the nitrogen lone pair into the aryl rings, leading to a dramatic influence on the nonlinear optical properties. Introduction of methoxy groups at the ortho positions of the TAA moiety has a larger influence on the molecular hyperpolarizability and dipole moment than the introduction of methoxy group at the para or meta positions. Our calculation results demonstrate how to improve the NLO properties of TAA based chromophores while meeting practical device requirements.

- Schiff base derivatives containing heterocycles with aggregation-induced emission and recognition ability
  Abstract:
  Three new Schiff base derivatives possessing various blue aggregation-induced emission (AIE) characteristics in tetrahydrofuran (THF)–water were synthesized. Their photophysical properties in solution, aqueous suspension, film and crystalline states, along with their relationships, were comparatively investigated. The crystallographic data for dye 1 and dye 3 indicated that the existence of multiple intermolecular hydrogen bonding interactions restricted intramolecular vibration and rotation. Moreover, the sizes and growth processes of particles with different water fractions were studied using a scanning electron microscope (SEM) and dynamic light scattering (DLS). The results showed that the small homogeneous particles, assembled in an ordered fashion with appropriate water contents, exhibited distinct AIE behavior. Moreover, in a THF–H2O (4 : 1, v/v) solution of HEPES (20 mM) buffer, dye 2 showed fluorescence turn-on sensing towards Cr3+ and Al3+ via chelation enhanced fluorescence (CHEF). The 2 : 1 stoichiometries of the sensor complexes (dye 2–Cr3+ and dye 2–Al3+) were calculated from Job plots based on fluorescence titrations.

- Steric Protected and Illumination-Activated Tumor Targeting Accessory for Endowing Drug-Delivery Systems with Tumor Selectivity
  Abstract:
An ABA-typed polymeric accessory is synthesized to endow traditional micelle-based drug carriers with an illumination-activated tumor specific intracellular drug-delivery capacity. The targeting function of this accessory can be effectively suppressed due to the hiding of ligands. After photo-irradiation, the cleavage of o-nitrobenzyl groups in the functional accessory leads to the stretch of PEG chains, resulting in activated tumor-targeting functions.

- Click Chemistry Plays a Dual Role in Biodegradable Polymer Design
  Abstract:
  Click chemistry plays a dual role in the design of new citrate-based biodegradable elastomers (CABEs) with greatly improved mechanical strength and easily clickable surfaces for biofunctionalization. This novel chemistry modification strategy is applicable to a number of different types of polymers for improved mechanical properties and biofunctionality.

- Selective Host–Guest Interactions of a Transformable Coordination Capsule/Tube with Fullerenes
  Abstract:
  An M₂L₄ coordination capsule or an M₂L₂ coordination tube was selectively formed by the combination of Hg²⁺ hinges and bent bipyridine ligands. The two structures reversibly interconvert at room temperature in response to modulation of the metal-to-ligand ratio and exhibit different host–guest interaction behavior. The capsule alone encapsulates large spherical molecules, fullerenes C₆₀ and C₇₀, and the bound guests are released upon capsule-to-tube transformation by the simple
addition of metal ions.

- Redox-Responsive Macroscopic Gel Assembly Based on Discrete Dual Interactions
  **Abstract:**

  The macroscopic self-assembly of polymeric hydrogels modified with β-cyclodextrin (βCD gel), ferrocene (Fc gel), and styrenesulfonic acid sodium salt (SSNa gel) was investigated. Under reductive conditions, the Fc gel selectively adhered to the βCD gel through a host-guest interaction. On the other hand, the oxidized ferrocenium (Fc+) gel selectively adhered to the SSNa gel through an ionic interaction under oxidative conditions. The adhesion strength was estimated by a tensile test. We finally succeeded in forming an ABC-type macroscopic assembly of all three gels through two discrete noncovalent interactions.

- Electrochemistry of Nanoparticles
  **Abstract:**

  Metal nanoparticles (NPs) find widespread application as a result of their unique physical and chemical properties. NPs have generated considerable interest in catalysis and electrocatalysis, where they provide a high surface area to mass ratio and can be tailored to promote particular reaction pathways. The activity of NPs can be analyzed especially well using electrochemistry, which probes interfacial chemistry directly. In this Review, we discuss key issues related to the electrochemistry of NPs. We highlight model studies that demonstrate exceptional control over the NP shape and size, or mass-transport conditions, which can provide key insights into the behavior of ensembles of NPs. Particular focus is on the challenge of ultimately measuring reactions at individual NPs, and relating the response to their structure, which is leading to imaginative experiments that have an impact on electrochemistry in general as well as broader surface and colloid science.

- Liquid crystal organization of self-assembling cyclic peptides

Abstract:
Self-assembling cyclic peptides decorated with mesogens form porous columnar mesophases in which, depending on the number of hydrocarbon chains, double or single channels are formed along each column.

- Ligation of anti-cancer drugs to self-assembling ultrashort peptides by click chemistry for localized therapy

Abstract:
Self-assembling ultrashort peptides from aliphatic amino acids were functionalized with platinum anti-cancer drugs by click chemistry. Oxaliplatin-derived hybrid peptide hydrogels with up to 40% drug loading were tested for localized breast cancer therapy. Stably injected gels showed significant tumor growth inhibition in mice and a better tolerance compared to the free platinum drug.

- Filming Biomolecular Processes by High-Speed Atomic Force Microscopy

Abstract:
This Review focuses on application studies of HS-AFM, in which dynamics of proteins and live cells are visualized. For application studies of HS-AFM on the dynamics of DNA and DNA-binding proteins. Here, we also describe the HS-AFM setup, substrate surfaces, and precautions to be considered in HS-AFM imaging experiments. Before these topics are described, the physical backgrounds of the
high imaging rate and low invasiveness are explained. In the last part of this Review, future prospects of HS-AFM studies are briefly outlined.

- Cyclic [4]Rotaxanes Containing Two Parallel Porphyrinic Plates: Toward Switchable Molecular Receptors and Compressors
  Abstract:

Twenty years ago, researchers considered the synthesis of simple rotaxanes a challenging task, but with the rapid development of this field, chemists now view these interlocking molecules as accessible synthetic targets. In a major advance for the field, researchers have developed transition metals or organic molecules as templating structures, making it easier to construct these molecular systems. In addition, chemists have found ways to introduce new functional groups, which have given these compounds new properties. Today researchers can also construct multirotaxanes consisting of several individual components, but the synthesis of the most complex structures remains challenging.

This Account primarily discusses the cyclic [4]rotaxanes incorporating porphyrins that the Strasbourg group has synthesized and studied during the past few years. These cyclic [4]rotaxanes consist of two rigid rods threaded through the four rings of two molecules of a bis-macrocycle, and the synthetic strategy used for making them relies on the copper(I)-driven “gathering-and-threading” reaction. The formation of the threaded precursors was mostly quantitative, and the quadruple stoppering reaction leading to the target compound produces high yields because of the efficient copper-catalyzed azide–alkyne cycloaddition (CuAAC) or click chemistry reaction. These rotaxanes behave as receptors for various ditopic guests. We prepared and studied two types of molecules: (i) a rigid compound whose copper(I) complex has a well-defined shape, with high selectivity for the guest geometry and (ii) a much more flexible [4]rotaxane host that could act as a distensible receptor. The rigid [4]rotaxane was crystallized, affording a spectacular X-ray structure that matched the expected chemical structure. In addition, metalation or demetalation of the rigid [4]rotaxane induces a drastic geometric rearrangement. The metal-free compound is flat without a binding pocket, while the copper-complexed species forms a rectangle-like structure. The removal of copper(I) also expels any complexed guest molecule, and this process is reversible, making the rigid porphyrinic [4]rotaxane a switchable receptor. The rigid [4]rotaxane was highly selective for short, ditopic guests in its copper(I)-complexed form, but the flexible copper(I)-complexed [4]rotaxane proved to be a versatile receptor. Its conformation can adjust to the size of the guest molecule similar to the induced fit mechanism that some enzymes employ with substrates.
Mitochondria have specialized ribosomes that have diverged from their bacterial and cytoplasmic counterparts. We have solved the structure of the yeast mitoribosomal large subunit using single-particle cryo–electron microscopy. The resolution of 3.2 angstroms enabled a nearly complete atomic model to be built de novo and refined, including 39 proteins, 13 of which are unique to mitochondria, as well as expansion segments of mitoribosomal RNA. The structure reveals a new exit tunnel path and architecture, unique elements of the E site, and a putative membrane docking site.

Quantum tunneling between two plasmonic resonators links nonlinear quantum optics with terahertz nanoelectronics. We describe the direct observation of and control over quantum plasmon resonances at length scales in the range 0.4 to 1.3 nanometers across molecular tunnel junctions made of two plasmonic resonators bridged by self-assembled monolayers (SAMs). The tunnel barrier width and height are controlled by the properties of the molecules. Using electron energy-loss spectroscopy, we directly observe a plasmon mode, the tunneling charge transfer plasmon, whose frequency (ranging from 140 to 245 terahertz) is dependent on the molecules bridging the gaps.