• Reversible electronic energy transfer: a means to govern excited-state properties of supramolecular systems
Abstract:

A strategy to manage energy, following light absorption, and modulate excited-state properties, including luminescence lifetimes of multicomponent photoactive systems, is presented. The intervening mechanism, which is illustrated through the use of bi-/multi-chromophoric molecules, relies on energy shuttling between different matched chromophores under kinetic and thermodynamic control. This tutorial review is destined to show supramolecular and materials chemists, spectroscopists and nanoscientists how to harness reversible electronic energy transfer in a predictable fashion in designer molecule-based systems.

• Cyclodextrin-based bioactive supramolecular assemblies
Abstract:

Cyclodextrins (CDs) are a class of cyclic oligosaccharides with six to eight D-glucose units linked by \( \alpha \) -1,4-glucose bonds, and their capability of forming stable complexes with various organic/inorganic/biological molecules and ions makes them attractive as building blocks for the construction of nano-scale supramolecular systems. This tutorial review deals with representative contributions in the construction and the structural characteristics of CD-based supramolecular assemblies as well as their interactions with biologically important substrates. This review is addressed to students and researchers interested in supramolecular chemistry, biochemistry and nanotechnology.

• Toward Controlling Folding in Synthetic Polymers: Fabricating and Characterizing Supramolecular Single-Chain Nanoparticles
Abstract:
We discuss in detail our facile method for producing supramolecular polymeric nanoparticles from the collapse of single polymer chains. A new family of poly(methyl methacrylate)-based nanoparticles confirm that our method is general and can be easily tuned toward a variety of applications. Thorough AFM characterization elucidates the conditions required to visualize single particles as well as complex assemblies of particles mediated by the evaporation of solvent. AFM studies also indicate that the intramolecular collapse resembles the cooperative folding process witnessed in biomacromolecules and that the particles possess a complex morphology that implies the internal organization of the UPy dimers used to induce the intramolecular collapse. Thermal studies support these observations in addition to confirming the applicability of this system in the fabrication of processable high-performance supramolecular materials.

- Covalent Cross-Linked Polymer Gels with Reversible Sol–Gel Transition and Self-Healing Properties
  Abstract:

Herein, we report a strategy of constructing novel reversible polymer gels based on dynamic covalent chemistry. By condensation of acylhydrazines at the two ends of a poly(ethylene oxide) (PEO) ($A_2$) with aldehyde groups in tris[(4-formylphenoxy)methyl]ethane ($B_3$), a network with acylhydrazone bonds as cross-links is generated. Acylhydrazone bonds are covalent in nature and, therefore, the polymer network should be stable under normal conditions as that of conventional covalent gels. But more importantly, acylhydrazone formation displays reversibility under mild conditions with acid catalysis, breaking down the network and regenerating the starting reagents. By adjusting the acidity of the system, this chemical gel reveals reversible sol–gel phase transitions. Moreover, the chemical gel possesses self-healing property based on the reversible breaking and regenerating of acylhydrazone bonds.

- Autonomous Silica Encapsulation and Sustained Release of Anticancer Protein
  Abstract:
We present a novel method for preparing a silica carrier for the sustained release of a proteinaceous pharmaceutical. This method makes use of the silicification activity of the protein itself, which autonomously formed a protein–silica composite upon simple incubation with a silica precursor. The composite was dissolved, and the encapsulated protein was released into a culture medium, thereby sustaining the protein’s activity for a long period of time.

- Delivery and Efficacy of a Cancer Drug as a Function of the Bond to the Gold Nanoparticle Surface
  Abstract:

  In this feature article, gold nanoparticle conjugates loaded with phthalocyanine-based PDT drugs are prepared and tested for delivery efficiency and PDT efficacy on HeLa cancer cells. It could be shown that the delivery and PDT outcome are strongly affected by the bond that links the drug load to the nanoparticle surface. Whereas labile amino adsorption to the Au nanoparticle surface allows for efficient drug release into the cancer cells and for efficient PDT, a covalent thiol bond to the Au nanoparticle leads to the delivery of the drug into cell vesicles, and no PDT effect is observed. This work highlights the importance of carefully choosing the interaction between drug molecules and the nanoparticle surface.

- A New Artificial β-Sheet That Dimerizes through Parallel β-Sheet Interactions
  Abstract:
This paper introduces a chemical model of a β-sheet that dimerizes through parallel β-sheet interactions in CDCl₃ solution. The model consists of two C-terminally linked dipeptides connected to a molecular template. ¹H NMR studies establish the β-sheet folding and dimerization of the model system. This system corroborates that linking two peptide strands and blocking one edge of the assembly creates soluble, easy-to-study systems that participate in the types of interactions that occur widely in peptide and protein aggregates.

- Cyclooligomerization of a Helix-Bearing Template into Macrocycles Bearing Multiple Helices

  Abstract:

  Cyclooligomerization was investigated for separating and spatially arranging helical peptides as discontinuous surfaces. Tetrapeptide H-[Ile-Ser-Lys(Ox)]-OH, containing a turn-inducing oxazole constraint, was connected through its lysine side chain via a β-alanine linker to the C-terminus of a two-turn helical nonapeptide Ac-(cyclo-4,8)-LRL[KARAD](Aib). The resulting helix-appended template was self-condensed and cyclized to a library of macrocycles (n = 2–6) containing multiple (2–6) helices. An NMR structure shows retention of α helicity in the cyclotrimer (n = 3).

- Exceptionally large positive and negative anisotropic thermal expansion of an organic crystalline material

  Abstract:

  In general, the relatively modest expansion experienced by most materials on heating is caused by increasing anharmonic vibrational amplitudes of the constituent atoms, ions or molecules. This phenomenon is called positive thermal expansion (PTE) and usually occurs along all three crystallographic axes. In very rare cases, structural peculiarities may give rise either to anomalously large PTE, or to negative thermal expansion (NTE, when lattice dimensions shrink with heating). As NTE and unusually large PTE are extremely uncommon for molecular solids, mechanisms that might give rise to such phenomena are poorly understood. Here we show that the packing arrangement of
a simple dumbbell-shaped organic molecule, coupled with its intermolecular interactions, facilitates a cooperative mechanical response of the three-dimensional framework to changes in temperature. A series of detailed structural determinations at 15-K intervals has allowed us to visualize the process at the molecular level. The underlying mechanism is reminiscent of a three-dimensional (3D) folding trellis and results in exceptionally large and reversible uniaxial PTE and biaxial NTE of the crystal. Understanding such mechanisms is highly desirable for the future design of sensitive thermomechanical actuators.

- Nanotribology the renaissance of friction
  
  Abstract:

500 years after the first studies on friction, the concepts of superlubricity, wearless sliding and friction control are being realized in laboratories and have become predictable by adequate modelling. The challenge now is to bridge the gap between what is known about these processes on the microscopic and macroscopic scales.

- Metallo-supramolecular diblock copolymers based on heteroleptic cobalt(III) and nickel(II) bis-terpyridine complexes
  
  Abstract:

Amphiphilic metallo-supramolecular diblock copolymers containing either a reversible cobalt(III) or nickel(II) heteroleptic bis-terpyridine complex at the junction between a polystyrene and a poly(ethylene oxide) block have been successfully prepared.

  
  Abstract:
Redox-driven mechanical movement, which has been achieved for a liquid-crystalline (LC) bistable [2]rotaxane in the LC phase, is accompanied by obvious electrochromism (electrochemically induced changes in color) of the material. The dumbbell-shaped LC [2]rotaxane with redox-active moieties, which interlocks with an ionic macrocycle, forms ordered redox-active condensed states.

- Self-Assembly of Discrete Homochiral, Helical, Hydrogen-Bonded Nanocages: From Vesicles to Microspheres and Tubules Capable of Gelating Solvents


Abstract:

The chiral tris-monodentate imidazolinyl ligands 1 a-c exhibit a strong tendency to form the discrete, helical [2+3] nanocages 3 ([1]2·2]) with tartaric acids 2. Circular dichroism (CD) spectra and theoretical calculations reveal that supramolecular handedness of capsul-like architectures is determined only by the chirality of the imidazolinyl ligands rather than tartaric acids. The chirality of imidazolinyl ligands is transferred to the helicity of the complexes through the directed hydrogen bonds between the N3 atom of imidazolene rings and the carboxyl of tartaric acids. These hydrogen-bonded nanocages can spontaneously self-assemble into spherical vesicles, during which the hydrogen bonding that arises from the hydroxyl groups of tartaric acids plays a crucial issue. The vesicles formed by [(5S,5S)-1a]2([2]2)3 (3 a) may further evolve into microspheres that gelate organic solvents after being aged at -20 °C for 24 h, and can also be unprecedentedly transformed to tubular assemblies capable of rigidifying the solvents when subjected to ultrasound irradiation.


Abstract:
Versatile concave receptors with binding properties that can be controlled by external stimuli are rare. Herein, we report on a calix[6]crypturea (1) that features two different binding sites in close proximity, that is, a tris(2-aminoethyl)amine (tren)-based tris-ureido cap that provides convergent hydrogen-bond-donor sites and a hydrophobic cavity suitable for the inclusion of organic guests. The binding properties of this heteroditopic receptor have been evaluated by NMR spectroscopic studies. Compound 1 behaves as a remarkably versatile host that strongly binds neutral molecules, anions, or contact ion pairs. Within each family of guests, compound 1 is able to discriminate between different guests with a high degree of selectivity. Indeed, neutral molecules that possess hydrogen-bond donor and acceptor groups, chloride anions, and linear ammonium ions associated to F- or Cl- are particularly well recognized. In comparison with all the related receptors, compound 1 displays several unique features: 1) charged or neutral species are also recognized in polar or protic solvents, 2) thanks to the flexibility of the calixarene structure, induced-fit processes allow the binding of large, biologically relevant ammonium salts such as neurotransmitters, and 3) the protonation of the basic cap leads to a positively charged receptor, 1-H+, which is reluctant to host anions and in which host properties are now governed by strong charge-dipole interactions with the guests. In other words, compound 1 presents an acid-base controllable tris-ureido recognition site protected by a hydrophobic corridor that can select guests through induced-fit processes. Thus, its versatile host properties can be allosterically controlled by protonation and selective guest-switching processes are possible. To illustrate all these remarkable features, a sophisticated three-pole supramolecular switch, based on the interconversion of host-guest systems displaying either charged or neutral guests, is described.

- Structure and Excitonic Coupling in Self-Assembled Monolayers of Azobenzene-Functionalized Alkanethiols

Abstract:

Optical properties and the geometric structure of self-assembled monolayers of azobenzene-functionalized alkanethiols have been investigated by UV/visible and near edge X-ray absorption fine structure spectroscopy in combination with density-functional theory. By attaching a trifluoro-methyl end group to the chromophore both the molecular tilt and twist angle of the azobenzene moiety are accessible. Based on this detailed structural analysis the energetic shifts observed in optical reflection spectroscopy can be qualitatively described within an extended dipole model. This substantiates sizable excitonic coupling among the azobenzene chromophores as an important mechanism that hinders trans to cis isomerization in densely packed self-assembled monolayers.
• Zinc-Catalyzed Reduction of Amides: Unprecedented Selectivity and Functional Group Tolerance
Abstract:

\[ \text{Cat. Zn(OAc)}_2 \rightarrow \begin{array}{c} \text{R} = \text{alkyl, aryl, heterocyclic, alicyclic} \\ \text{R}^1, \text{R}^2 = \text{alkyl, heterocyclic, alicyclic} \end{array} \]

A novel zinc-catalyzed reduction of tertiary amides was developed. This system shows remarkable chemoselectivity and substrate scope tolerating ester, ether, nitro, cyano, azo, and keto substituents.

• Geometry and Electronic Coupling in Perylenediimide Stacks: Mapping Structure–Charge Transport Relationships
Abstract:

The binding energy and electronic coupling of perylenediimide (PDI) \( \pi \)-stacked dimers were calculated using M06-2X/6-31++G** as a function of stacking geometry. Due to shallow minima in the potential energy surface, electronic coupling can vary by over an order of magnitude among energetically accessible geometries. The coupling was then determined for 20 PDI derivatives with various substitutions at the imide region, and several were identified as the most promising candidates for organic thin film transistors (OTFTs). This strategy of side-by-side comparison of binding energy and electronic coupling may prove useful for other \( \pi \)-stacked OTFTs such as pentacene and poly(thiophene) derivatives.

• A Bis-exTTF Macroyclic Receptor That Associates \( \text{C}_{60} \) with Micromolar Affinity
Abstract:
An exTTF-based macrocyclic receptor that associates $C_{60}$ with a binding constant $>10^6$ M$^{-1}$ in chlorobenzene at room temperature is described. This represents an improvement of 3 orders of magnitude with respect to the previous examples of exTTF-based receptors and one of the highest binding constants toward $C_{60}$ reported to date.

- **Iminium–Allenamine Cascade Catalysis: One-Pot Access to Chiral 4HChromenes by a Highly Enantioselective Michael–Michael Sequence**
  **Abstract:**
  ![Iminium–Allenamine Cascade Catalysis](image)

  **Taking the Michael–Michael:** A cascade Michael-Michael reaction of aryl or alkyl alkynals, involving an unprecedented iminium-allenamine sequence, is efficiently catalyzed by a chiral diphenylprolinol TBDMS ether, and affords highly functionalized 4H-chromenes in high yields. TBDMS=tert-butyldimethylsilyl.

- **Nanoscale Flexibility Parameters of Alzheimer Amyloid Fibrils Determined by Electron Cryo-Microscopy**
  **Abstract:**
  ![Nanoscale Flexibility Parameters](image)

  **Versatile nanomaterial:** Unusually high nanoscale flexibility was displayed by amyloid fibils in electron microscopy studies (see picture). This finding is relevant for understanding amyloid pathogenicity and for potential biotechnological applications.

- **Predicting the reaction coordinates of millisecond light-induced conformational changes in photoactive yellow protein**
  **Abstract:**
Understanding the dynamics of large-scale conformational changes in proteins still poses a challenge for molecular simulations. We employ transition path sampling of explicit solvent molecular dynamics trajectories to obtain atomistic insight in the reaction network of the millisecond timescale partial unfolding transition in the photocycle of the bacterial sensor photoactive yellow protein. Likelihood maximization analysis predicts the best model for the reaction coordinates of each substep as well as tentative transition states, without further simulation. We find that the unfolding of the α-helical region 43–51 is followed by sequential solvent exposure of both Glu46 and the chromophore. Which of these two residues is exposed first is correlated with the presence of a salt bridge that is part of the N-terminal domain. Additional molecular dynamics simulations indicate that the exposure of the chromophore does not result in a productive pathway. We discuss several possibilities for experimental validation of these predictions. Our results open the way for studying millisecond conformational changes in other medium-sized (signaling) proteins.

- Chemoenzymatic synthesis of differentially protected 3-deoxysugars
  Abstract:

3-Deoxysugars are important constituents of complex carbohydrates. For example, 2-keto-3-deoxy-D-manno-octulosonic acid (KDO) is an essential component of lipopolysaccharides in Gram-negative bacteria, 2-keto-3-deoxy-D-glycero-D-galactonulosonic acid (KDN) is widely found in carbohydrates of the bacterial cell wall and in lower vertebrates, and sialic acid is a common cap of mammalian glycoproteins. Although ready access to such sugars would benefit the creation of vaccine candidates, antibiotics and small-molecule drugs, their chemical synthesis is difficult. Here we present a simple chemoenzymatic method for preparing differentially protected 3-deoxysugar derivatives from readily available starting materials. It exploits the promiscuous aldolase activity of the enzyme macrophomate synthase (MPS) to add pyruvate enolate diastereoselectively to a wide range of structurally complex aldehydes. A short synthesis of KDN illustrates the utility of this approach. Enzyme promiscuity, which putatively fosters large functional leaps in natural evolution, has great promise as a source of synthetically useful catalytic transformations.