- Expedient Enantioselective Synthesis of the Δ4-Oxocene Cores of (+)-Laurencin and (+)-Prelaureatin
  Abstract:
  An expedient enantioselective synthesis of the Δ4-oxocene cores present in (+)-laurencin and (+)-prelaureatin was accomplished in eight steps via a novel one-pot regio- and stereoselective ring cyclization-fragmentation-expansion cascade from the tetrahydrofuran precursors which were prepared by stereocontrolled cyclization from vinylsilanes. This process is highlighted by an intramolecular oxo carbenoid insertion and a beta-silyl fragmentation sequence.

- Palladium-Catalyzed Carbo-Heterofunctionalization of Alkenes for the Synthesis of Oxindoles and Spirooxindoles
  Abstract:
  A palladium-catalyzed oxidative carbo-heterofunctionalization of aniline derivatives involving concomitant direct C-H functionalization and C-X bond formation was developed. By simply changing the reaction conditions (solvent and catalyst), either 3,3′-disubstituted oxindole or spirooxindole was accessible from the same starting material.

- Electrically Polarized Biphasic Calcium Phosphates: Adsorption and Release of Bovine Serum Albumin
  Abstract:
In this study, we applied electrical polarization technique to increase adsorption and control protein release from biphasic calcium phosphate (BCP). Three different biphasic calcium phosphate (BCP) composites, with hydroxyapatite (HAp) and β-tricalcium phosphate (β-TCP), were processed and electrically polarized. Our study showed that stored charge was increased in the composites with the increase in HAp percentage. Adsorption of bovine serum albumin (BSA), as a model protein, on the poled as well as unpoled surfaces of the composites was studied. The highest amount of BSA adsorption was obtained on positively poled surfaces of each composite. Adsorption isotherm study suggested a multilayer adsorption of BSA on the BCP composites. The effect of electrical polarization on BSA release kinetics from positively charged BCP surfaces was studied. A gradual increase in percent BSA release from positively charged BCP surfaces with decreasing stored charge was observed. Our study showed that the BCP based composites have the potential to be used as a drug or growth factor delivery vehicle.

- Evidence of Intercolumnar π–π Stacking Interactions in Amino-Acid-Based Low-Molecular-Weight Organogels
  Abstract:

A comparative IR and NMR study of two low-molecular-weight organogels (LMWGs) based on aminoacid derivatives let us point out the hierarchy of the gelation assembly process. Different association states of corresponding organogelator molecules can be observed leading to the supramolecular organization of gel. A first hydrogen bond network of gelators leads to the formation of “head-to-tail” stacking-up, which can be assembled afterward one to the other by π–π stacking interactions. These small supramolecular aggregates (incipient precursor) are still visible in NMR spectra, and they represent, for example, 36% of the total amount of gelator in the case of the l-phenylalanine derivative (gelator 1) at 1 wt % in toluene. Finally, in the last step, the incipient precursor tends to form the expected 3D fibrillar network responsible for the gelation phenomenon.
Temperature-dependent IR and NMR experiments allowed us to identify these different states clearly.

- **Surface Modification of Self-Assembled One-Dimensional Organic Structures: White-Light Emission and Beyond**
  **Abstract:**

  Surface modification is an important method to functionalize micro-/nanostructures, but substrates are mainly confined to robust inorganic compounds. We develop here a facile method to modify the surface of a fragile organic 1D microstructure. The bulk molecules and surface modifier were designed with orthogonal solubility to protect the molecular crystals from destruction under the reaction conditions. As a proof of concept, white-light-emitting 1D microstructures were obtained by grafting red chromophores onto the surface of self-assembled blue-emissive microwires via a heterophase SN2 reaction. Spatial distribution of the two species is visualized by fluorescent lifetime mapping, which reveals a core–shell structure. The ability to postfunctionalize organic 1D structures enables many applications, where the surface property plays key roles, such as an organic P–N junction and a biosensor.

- **Guanine- and Potassium-Based Two-Dimensional Coordination Network Self-Assembled on Au(111)**
  **Abstract:**

  In this study, through the choice of the well-known G–K biological coordination system, bioligand–alkali metal coordination has for the first time been brought onto an inert Au(111) surface. Using the interplay between high-resolution scanning tunneling microscopy and density functional
theory calculations, we show that the mobile G molecules on Au(111) can effectively coordinate with the K atoms, resulting in a metallosupramolecular porous network that is stabilized by a delicate balance between hydrogen bonding and metal–organic coordination.

- Stable Cyclic Carbenes and Related Species beyond Diaminocarbenes
  Abstract:

  ![Diagram of cyclic carbenes](image)

  The success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of various systems. Spectacular results in this area have been achieved using cyclic diaminocarbenes (NHCs) as a result of their strong σ-donor properties. Although it is possible to cursorily tune the structure of NHCs, any diversity is still far from matching their phosphorus-based counterparts, which is one of the great strengths of the latter. A variety of stable acyclic carbenes are known, but they are either reluctant to bind metals or they give rise to fragile metal complexes. During the last five years, new types of stable cyclic carbenes, as well as related carbon-based ligands (which are not NHCs), and which feature even stronger σ-donor properties have been developed. Their synthesis and characterization as well as the stability, electronic properties, coordination behavior, and catalytic activity of the ensuing complexes are discussed, and comparisons with their NHC cousins are made.

- Graphene Oxide Framework Materials: Theoretical Predictions and Experimental Results
  Abstract:

  ![Diagram of graphene oxide framework](image)

  A promising storage medium for hydrogen and other gases is a graphene oxide framework (GOF) that consists of layers of GO connected by benzene-1,4-diboronic acid (B14DBA) pillars (see picture). Theoretical predictions and the initial experimental results are presented for this cheap and environmentally friendly building block for nanoporous materials with better gas adsorption properties.

- A new benzimidazole/carbazole hybrid bipolar material for highly efficient deep-blue electrofluorescence, yellow–green electrophosphorescence, and two-color-based white OLEDs
  Abstract:
The bipolar molecule CPhBzIm exhibits an excellent solid state photoluminescence quantum yield ($\Phi_{PL} = 69\%$), triplet energy ($E_T = 2.48$ eV), and bipolar charge transport ability ($\mu_h \approx \mu_e \approx 10^{-6}$–$10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$). We have used it to fabricate a non-doped deep-blue organic light emitting diode (OLED) exhibiting promising performance [$\eta_{ext} = 3\%$; CIE = (0.16, 0.05)] and to serve as host material for a yellow–green phosphorescent OLED [$\eta_{ext} = 19.2\%$; CIE = (0.42, 0.56)]. Exploiting these dual roles, we used CPhBzIm in a simple singly doped, two-color-based white OLED ($\eta_{ext} = 7\%$; CIE = 0.31, 0.33).

- **Nano-Layered Microneedles for Transcutaneous Delivery of Polymer Nanoparticles and Plasmid DNA**
  **Abstract:**

  *Multilayer-coated microneedles* achieve transcutaneous delivery of plasmid DNA to the viable epidermis. Cy3-labeled plasmid DNA encoding luciferase (yellow) is deposited on biodegradable microneedle arrays through multilayer self-assembly and then delivered to the skin by microneedle application to achieve colocalization with Langerhans dendritic cells (MHC II-GFP–green).

- **Click Polymerization: Progresses, Challenges, and Opportunities**
  **Abstract:**
Chemical transformations of small molecules have served as a rich source of reactions for the development of new polymerization processes, and “click” reaction has the potential to become a powerful polymerization technique. We herein give a brief account of the research efforts devoted to the development of click reaction into a new polymerization process. Remarkable progresses have been made in recent years in the exploration of metal-mediated and metal-free click polymerization systems and in the syntheses of linear and hyperbranched polytriazoles with regioregular molecular structures and advanced functional properties. We also discuss the existing limitations and challenges as well as the promising opportunities and directions in fostering the click polymerization into a versatile tool for the construction of new macromolecules with well-defined structures and multifaceted functionalities.

- Renewable Rosin Acid-Degradable Caprolactone Block Copolymers by Atom Transfer Radical Polymerization and Ring-Opening Polymerization

Abstract:

Renewable rosin acid-degradable caprolactone block copolymers were prepared by atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP). Two-step sequential polymerization using either poly(2-acryloyloxyethyl dehydroabietic carboxylate)-OH (PAEDA-OH) or poly(ε-caprolactone)-Br (PCL-Br) as macroinitiators resulted in well-defined block copolymers with low polydispersity. One-pot polymerization was carried out with three different sequential feeds of AEDA and ε-CL monomers. The control of one-pot polymerization depended on the interactions of
coexisting ATRP catalysts and ROP catalysts. While the minimal interactions between copper(I) and tin(II) catalysts produced well-defined block copolymers, excess copper(II) or tin(II) led to the formation of block copolymers with polydispersity >1.5. It was suggested that the tin(II) catalysts reduced the persistent radicals copper(II) of ATRP, leading to a poorly controlled polymerization. PCL segments of the block copolymers exhibited excellent degradability under acidic conditions. Thermal behaviors of these block copolymers showed a strong dependence of polymer compositions due to the possible crystallization of the PCL block.

- Supramolecular surface-confined architectures created by self-assembly of triangular phenylene–ethynylene macrocycles via van der Waals interaction
  Abstract:

At the liquid/graphite interface triangular and rhombic phenylene–ethynylene macrocycles substituted by alkyl chains self-assemble to form porous two-dimensional (2D) molecular networks of honeycomb and Kagomé types, respectively, or close-packed non-porous structures via alkyl chain interdigitation as the directional intermolecular linkages. Factors that affect the formation of the 2D molecular networks, such as alkyl chain length, solvent, solute concentration, and co-adsorption of guest molecules, were elucidated through a systematic study. For the porous networks, various molecules and molecular clusters were adsorbed in the pores reflecting the size and shape complementarity, exploring a new field of 2D host–guest chemistry.

- A self-assembled, luminescent europium cholate hydrogel: a novel approach towards lanthanide sensitization
  Abstract:

We propose a new self-assembly based strategy for the design of novel lanthanide based luminescent materials. In this approach a europium hydrogel is prepared and sensitization is achieved by doping the gel with pyrene in a non-coordinated fashion.

- Functional cyclophanes: Promising hosts for optical biomolecular recognition
  Abstract:
Cyclophanes possess a defined cavity size and are efficient in encapsulating and stabilising guest molecules inside the cavity through various non-covalent interactions. This unique property of the cyclophanes has been widely exploited for the development of selective probes for a variety of guest molecules. The present tutorial review highlights the use of various interesting functionalised cyclophane architectures for the sensitive and selective optical recognition of important biomolecules.

- Recent advances in the use of temporary silicon tethers in metal-mediated reactions
  Abstract:

  This tutorial review describes the use of temporary silicon tethers in metal-mediated organic reactions, a strategy which although well-established in traditional organic synthesis is still a blossoming field in the organometallic arena. The benefits of silicon-tethering are manifold: the reactivity, selectivity, and efficiency of organometallic processes can all be dramatically enhanced, often with unique regio- and stereochemical outcomes compared to the analogous intermolecular transformations. In addition, the residual silicon functionality can undergo a wide range of chemistry subsequent to the tethered reaction, creating further synthetic opportunities.

- Enhanced Adsorption Affinity of Anionic Perylene-Based Surfactants towards Smaller-Diameter SWCNTs
  Abstract:
We present evidence from multiple characterization methods, such as emission spectroscopy, zeta potential, and analytical ultracentrifugation, to shed light on the adsorption behavior of synthesized perylene surfactants on single-walled carbon nanotubes (SWCNTs). On comparing dispersions of smaller-diameter SWCNTs prepared by using cobalt–molybdenum catalysis (CoMoCAT) with the larger-diameter SWCNTs prepared by high-pressure carbon monoxide decomposition (HiPco), we find that the CoMoCAT–perylene surfactant dispersions are characterized by more negative zeta potentials, and higher anhydrous specific volumes (the latter determined from the sedimentation coefficients by analytical ultracentrifugation), which indicates an increased packing density of the perylene surfactants on nanotubes of smaller diameter. This conclusion is further supported by the subsequent replacement of the perylene derivatives from the nanotube sidewall by sodium decyl benzene sulfonate (SDBS), which first occurs on the larger-diameter nanotubes. The enhanced adsorption affinity of the perylene surfactants towards smaller-diameter SWCNTs can be understood in terms of a change in the supramolecular arrangement of the perylene derivatives on the scaffold of the SWCNTs. These findings represent a significant step forward in understanding the noncovalent interaction of π-surfactants with carbon nanotubes, which will enable the design of novel surfactants with enhanced selectivity for certain nanotube species.

- Tuning the HOMO Energy Levels of Organic Dyes for Dye-Sensitized Solar Cells Based on Br−/Br3− Electrolytes
  Abstract:

A series of novel metal-free organic dyes TC301–TC310 with relatively high HOMO levels were synthesized and applied in dye-sensitized solar cells (DSCs) based on electrolytes that contain Br−/Br3− and I−/I3−. The effects of additive Li+ ions and the HOMO levels of the dyes have an important influence on properties of the dyes and performance of DSCs. The addition of Li+ ions in electrolytes can broaden the absorption spectra of the dyes on TiO2 films and shift both the LUMO levels of the dyes and the conduction band of TiO2, thus leading to the increase of Jsc and the decrease of Voc. Upon using Br−/Br3− instead of I−/I3−, a large increase of Voc is attributed to the enlarged energy difference between the redox potentials of electrolyte and the Fermi level of TiO2 as well as the suppressed electron recombination. Incident photon to current efficiency (IPCE) action spectra, electrochemical impedance spectra, and nanosecond laser transient absorption reveal that both the electron collection yields and the dye regeneration yields (Φr) depend on the potential difference (the driving forces) between the oxidized dyes and the Br−/Br3− redox couple. For the dyes for which the HOMO levels are more positive than the redox potential of Br−/Br3− sufficient driving forces lead to the longer effective electron-diffusion lengths and almost the same efficient dye regenerations, whereas for the dyes for which the HOMO levels are similar to the redox potential of Br−/Br3−, insufficient driving forces lead to shorter effective electron-diffusion lengths and inefficient dye regenerations.
• Photocatalytically active complexes that chemically and autonomously regenerate


Abstract:

Naturally occurring photosynthetic systems use elaborate pathways of self-repair to limit the impact of photo-damage. Here, we demonstrate a complex consisting of two recombinant proteins, phospholipids and a carbon nanotube that mimics this process. The components self-assemble into a configuration in which an array of lipid bilayers aggregate on the surface of the carbon nanotube, creating a platform for the attachment of light-converting proteins. The system can disassemble upon the addition of a surfactant and reassemble upon its removal over an indefinite number of cycles. The assembly is thermodynamically metastable and can only transition reversibly if the rate of surfactant removal exceeds a threshold value. Only in the assembled state do the complexes exhibit photocatalytic activity. We demonstrate a regeneration cycle that uses surfactant to switch between assembled and disassembled states, resulting in an increased photoconversion efficiency of more than 300% over 168 hours and an indefinite extension of the system lifetime.

• Pore opening and closing of a pentameric ligand-gated ion channel


Abstract:

Nerve signaling in humans and chemical sensing in bacteria both rely on the controlled opening and closing of the ion-conducting pore in pentameric ligand-gated ion channels. With the help of a multiscale simulation approach that combines mixed elastic network model calculations with molecular dynamics simulations, we study the opening and closing of the pore in Gloeobacter violaceus channel GLIC at atomic resolution. In our simulations of the GLIC transmembrane domain, we first verify that the two endpoints of the transition are open and closed to sodium ion...
conduction, respectively. We then show that a two-stage tilting of the pore-lining helices induces cooperative drying and iris-like closing of the channel pore. From the free energy profile of the gating transition and from unrestrained simulations, we conclude that the pore of the isolated GLIC transmembrane domain closes spontaneously. The mechanical work of opening the pore is performed primarily on the M2-M3 loop. Strong interactions of this short and conserved loop with the extracellular domain are therefore crucial to couple ligand binding to channel opening.

- Small molecules of different origins have distinct distributions of structural complexity that correlate with protein-binding profiles


Abstract:

Using a diverse collection of small molecules generated from a variety of sources, we measured protein-binding activities of each individual compound against each of 100 diverse (sequence-unrelated) proteins using small-molecule microarrays. We also analyzed structural features, including complexity, of the small molecules. We found that compounds from different sources (commercial, academic, natural) have different protein-binding behaviors and that these behaviors correlate with general trends in stereochemical and shape descriptors for these compound collections. Increasing the content of \( sp^3 \)-hybridized and stereogenic atoms relative to compounds from commercial sources, which comprise the majority of current screening collections, improved binding selectivity and frequency. The results suggest structural features that synthetic chemists can target when synthesizing screening collections for biological discovery. Because binding proteins selectively can be a key feature of high-value probes and drugs, synthesizing compounds having features identified in this study may result in improved performance of screening collections.