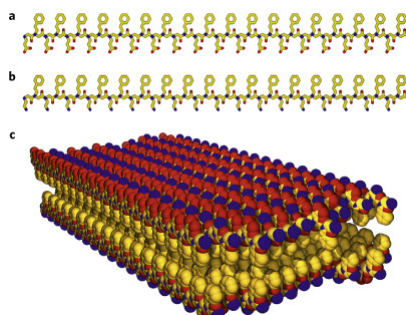


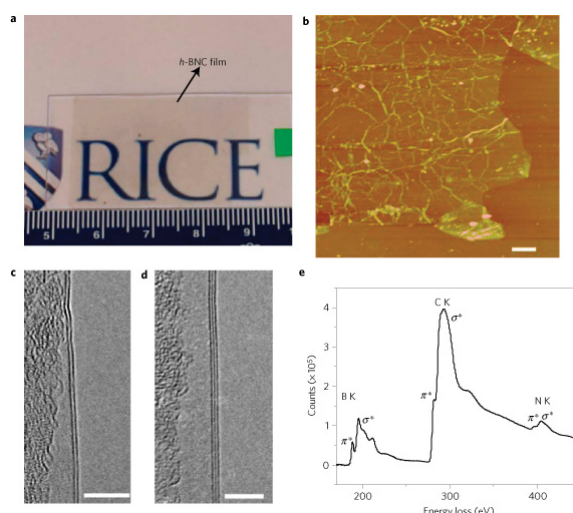
- Free-floating ultrathin two-dimensional crystals from sequence-specific peptoid polymers
Nam, K. T.; Shelby, S. A.; Choi, P. H.; Marciel, A. B.; Chen, R.; Tan, L.; Chu, T. K.; Mesch, R. A.; Lee, B.-C.; Connolly, M. D.; Kisielowski, C.; Zuckermann, R. N. *Nature Materials* **2010**, 9, 454 – 460.

1

Abstract:

The design and synthesis of protein-like polymers is a fundamental challenge in materials science. A biomimetic approach is to explore the impact of monomer sequence on non-natural polymer structure and function. We present the aqueous self-assembly of two peptoid polymers into extremely thin two-dimensional (2D) crystalline sheets directed by periodic amphiphilicity, electrostatic recognition and aromatic interactions. Peptoids are sequence-specific, oligo-*N*-substituted glycine polymers designed to mimic the structure and functionality of proteins. Mixing a 1:1 ratio of two oppositely charged peptoid 36mers of a specific sequence in aqueous solution results in the formation of giant, free-floating sheets with only 2.7 nm thickness. Direct visualization of aligned individual peptoid chains in the sheet structure was achieved using aberration-corrected transmission electron microscopy. Specific binding of a protein to ligand-functionalized sheets was also demonstrated. The synthetic flexibility and biocompatibility of peptoids provide a flexible and robust platform for integrating functionality into defined 2D nanostructures.

- Atomic layers of hybridized boron nitride and graphene domains
Ci, L.; Song, L.; Jin, C.; Jariwala, D.; Wu, D.; Li, Y.; Srivastava, A.; Wang, Z. F.; Storr, K.; Balicas, L.; Liu, F.; Ajayan, P. M. *Nature Materials* **2010**, 9, 430 – 435.

Abstract:

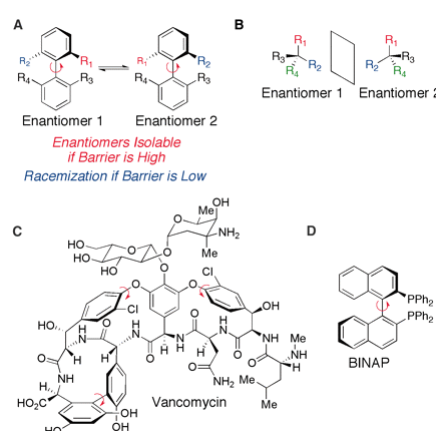
Two-dimensional materials, such as graphene and monolayer hexagonal BN (*h*-BN), are attractive for demonstrating fundamental physics in materials and potential applications in next-generation electronics. Atomic sheets containing hybridized bonds involving elements B, N and C over wide

compositional ranges could result in new materials with properties complementary to those of graphene and *h*-BN, enabling a rich variety of electronic structures, properties and applications. Here we report the synthesis and characterization of large-area atomic layers of *h*-BNC material, consisting of hybridized, randomly distributed domains of *h*-BN and C phases with compositions ranging from pure BN to pure graphene. Our studies reveal that their structural features and bandgap are distinct from those of graphene, doped graphene and *h*-BN. This new form of hybrid *h*-BNC material enables the development of bandgap-engineered applications in electronics and optics and properties that are distinct from those of graphene and *h*-BN.

- Dynamic Kinetic Resolution of Biaryl Atropisomers via Peptide-Catalyzed Asymmetric Bromination

Gustafson, J. L.; Lim, D.; Miller, S. J. *Science* **2010**, 328, 1251 – 1255.

Abstract:

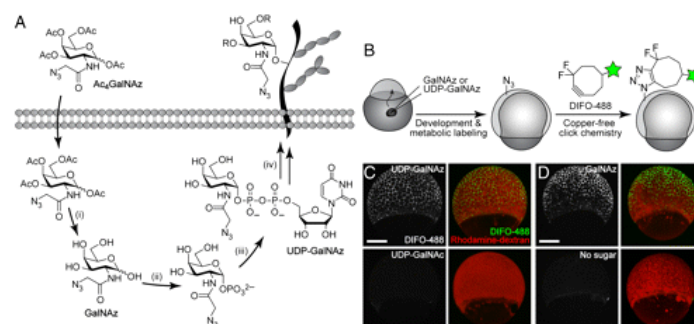


Despite the widespread use of axially chiral, or atropisomeric, biaryl ligands in modern synthesis and the occurrence of numerous natural products exhibiting axial chirality, few catalytic methods have emerged for the direct asymmetric preparation of this compound class. Here, we present a tripeptide-derived small-molecule catalyst for the dynamic kinetic resolution of racemic biaryl substrates. The reaction proceeds via an atropisomer-selective electrophilic aromatic substitution reaction using simple bromination reagents. The result is an enantioselective synthesis that delivers chiral nonracemic biaryl compounds with excellent optical purity and good isolated chemical yields (in most cases a >95:5 enantiomer ratio and isolated yields of 65 to 87%). A mechanistic model is advanced that accounts for the basis of selectivity observed.

- Visualizing enveloping layer glycans during zebrafish early embryogenesis

Baskina, J. M.; Dehnerta, K. W.; Laughlina, S. T.; Amacherb, S. L.; Bertozzi, C. R. *Proc. Nat. Acad. Sci.* **2010**, 107, 10360-10365.

Abstract:

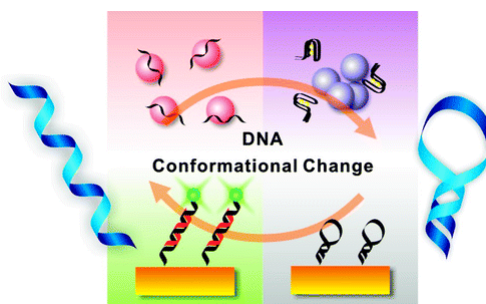


Developmental events can be monitored at the cellular and molecular levels by using noninvasive imaging techniques. Among the biomolecules that might be targeted for imaging analysis, glycans occupy a privileged position by virtue of their primary location on the cell surface. We previously described a chemical method to image glycans during zebrafish larval development; however, we were unable to detect glycans during the first 24 hours of embryogenesis, a very dynamic period in development. Here we report an approach to the imaging of glycans that enables their visualization in the enveloping layer during the early stages of zebrafish embryogenesis. We microinjected embryos with azidosugars at the one-cell stage, allowed the zebrafish to develop, and detected the metabolically labeled glycans with copper-free click chemistry. Mucin-type O-glycans could be imaged as early as 7 hours postfertilization, during the gastrula stage of development. Additionally, we used a nonmetabolic approach to label sialylated glycans with an independent chemistry, enabling the simultaneous imaging of these two distinct classes of glycans. Imaging analysis of glycan trafficking revealed dramatic reorganization of glycans on the second time scale, including rapid migration to the cleavage furrow of mitotic cells. These studies yield insight into the biosynthesis and dynamics of glycans in the enveloping layer during embryogenesis and provide a platform for imaging other biomolecular targets by microinjection of appropriately functionalized biosynthetic precursors.

- Target-Responsive Structural Switching for Nucleic Acid-Based Sensors

Li, D.; Song, S.; Fan, C. *Acc. Chem. Res.* **2010**, *43*, 631–641.

Abstract:



Interest in the development of sensitive, selective, rapid, and cost-effective biosensors for biomedical analysis, environmental monitoring, and the detection of bioterrorism agents is rapidly increasing. A classic biosensor directly transduces ligand–target binding events into a measurable physical readout. More recently, researchers have proposed novel biosensing strategies that couple ligand-induced structural switching of biomolecules with advanced optical and electronic transducers. This approach has proven to be a highly general platform for the development of new biosensors. In this Account, we describe a series of electrochemical and optical nucleic acid sensors that use target-responsive DNA structures.

By employing surface-confined DNA structures with appropriate redox labels, we can monitor target-induced structural switching of DNA or aptamer-specific small molecule probes by measuring electrochemical currents that are directly associated with the distance between the redox label and the electrode surface. We have also demonstrated significant improvements in sensing performance through optimization of the DNA self-assembly process at electrode surfaces or the introduction of nanomaterial-based signal amplification. Alternatively, gold nanoparticles interact differently with folded and unfolded DNA structures, which provides a visual method for detecting target-induced structural switching based on the plasmonic change of gold nanoparticles. This novel method using gold nanoparticles has proven particularly suitable for the detection of a range of small-molecule targets (e.g., cocaine) and environmentally toxic metal ions (e.g., Hg^{2+}). Rational sequence design of

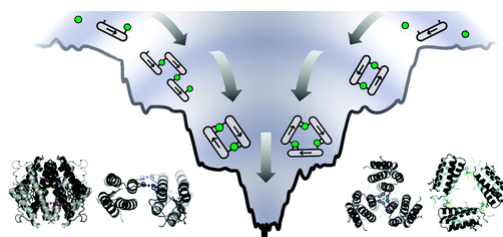
DNA aptamers improves the sensitivity and increases the reaction kinetics. Recently, we have also designed microfluidic devices that allow rapid and portable mercury detection with the naked eye.

This Account focuses on the use of bulk and nanoscale gold and DNA/aptamer molecules. We expect that researchers will further expand the analyte spectrum and improve the sensitivity and selectivity of nucleic acid sensors using functional biomolecules, such as DNazymes, peptide aptamers and engineered proteins, and nanomaterials of different sizes, dimensions and compositions, such as carbon nanotubes, graphene, silicon nanowires, and metal nanoparticles or nanorods.

- Metal-Directed Protein Self-Assembly

Salgado, E. N.; Radford, R. J.; Tezcan, F. A. *Acc. Chem. Res.* **2010**, *43*, 661–672.

Abstract:



Proteins are nature's premier building blocks for constructing sophisticated nanoscale architectures that carry out complex tasks and chemical transformations. Some 70%–80% of all proteins are thought to be permanently oligomeric; that is, they are composed of multiple proteins that are held together in precise spatial organization through noncovalent interactions. Although it is of great fundamental interest to understand the physicochemical basis of protein self-assembly, the mastery of protein–protein interactions (PPIs) would also allow access to novel biomaterials with nature's favorite and most versatile building block. In this Account, we describe a new approach we have developed with this possibility in mind, metal-directed protein self-assembly (MDPSA), which utilizes the strength, directionality, and selectivity of metal–ligand interactions to control PPIs.

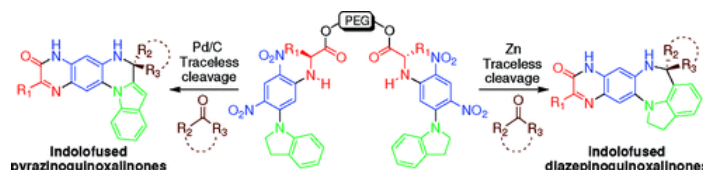
At its core, MDPSA is inspired by supramolecular coordination chemistry, which exploits metal coordination for the self-assembly of small molecules into discrete, more-or-less predictable higher order structures. Proteins, however, are not exactly small molecules or simple metal ligands: they feature extensive, heterogeneous surfaces that can interact with each other and with metal ions in unpredictable ways. We begin by first describing the challenges of using entire proteins as molecular building blocks. We follow with an examination of our work on a model protein (cytochrome *cb₅₆₂*), highlighting challenges toward establishing ground rules for MDPSA as well as progress in overcoming these challenges.

Proteins are also nature's metal ligands of choice. In MDPSA, once metal ions guide proteins into forming large assemblies, they are by definition embedded within extensive interfaces formed between protein surfaces. These complex surfaces make an inorganic chemist's life somewhat difficult, yet they also provide a wide platform to modulate the metal coordination environment through distant, noncovalent interactions, exactly as natural metalloproteins and enzymes do. We describe our computational and experimental efforts toward restructuring the noncovalent interaction network formed between proteins surrounding the interfacial metal centers. This approach, of metal templating followed by the redesign of protein interfaces (metal-templated interface redesign, MeTIR), not only provides a route to engineer de novo PPIs and novel metal coordination environments but also suggests possible parallels with the evolution of metalloproteins.

- Multistep Microwave-Assisted Divergent Synthesis of Indolo-Fused Pyrazino-/Diazepinoquinoxalinones on PEG Support

Lai, J.-J.; Salunke, D.B.; Sun, C.-M. *Org. Lett.* **2010**, 12, 2174–2177.

Abstract:

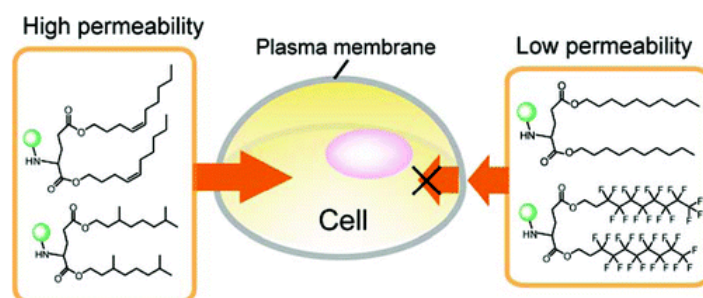


Synthesis of amino acid and indoline-substituted dinitrobenzene on a soluble polymer support (**PEG**) and its further reductive double-ring closure to afford structurally diverse indolo-fused pyrazino-/diazepinoquinoxalinones is described. Traceless synthesis of quinoxalinones coupled with application of the Pictet–Spengler-type condensation reaction furnished these novel scaffolds. These hitherto novel heterocycles are synthesized in shorter times under microwave irradiation conditions in comparison with that of classical reaction conditions.

- Influence of Hydrophobic Structures on the Plasma Membrane Permeability of Lipidlike Molecules

Niikura, K.; Nambara, K.; Okajima, T.; Matsuo Y.; Ijiro, K. *Langmuir* **2010**, 26, 9170–9175.

Abstract:

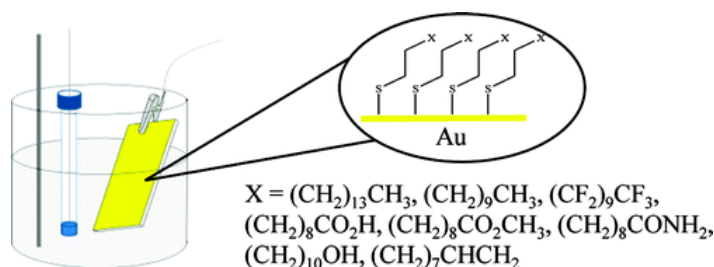


A series of FITC-labeled hydrophobic molecules (**1–8**) were prepared, and their cellular uptakes have been investigated using cell-cycle-synchronized HeLa cells. The cellular membrane permeability of compounds strongly depended on both the chemical structure and the cell-cycle phase. In the G1/S phase, branched hydrocarbon-containing **3** and *cis*-olefin-containing **2** and **8** were efficiently internalized into cells by passive diffusion. In contrast, linear alkyl chain-containing **1** and **7** were retained on the membrane without rapid internalization. In the M phase, rapid permeation was suppressed for all molecules.

- Compatibility of ω -Functionality in the Electrochemically Directed Self-Assembly of Monolayers on Gold from Alkyl Thiosulfates

Labukas, J. P.; Drake T. J. H.; Ferguson, G. S. *Langmuir* **2010**, 26, 9497–9505.

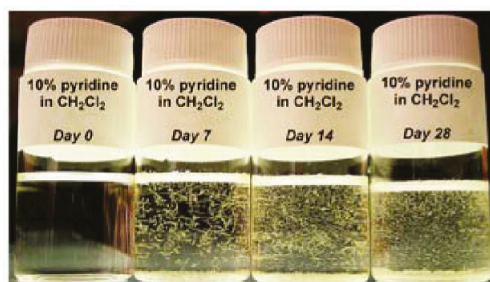
Abstract:



Self-assembled monolayers were formed on gold electrochemically from ω -functionalized alkyl thiosulfates (Bunte salts). The resulting SAMs were characterized using X-ray photoelectron spectroscopy (XPS), contact-angle goniometry, and ellipsometry. A range of terminal functionality was examined, including CH_3 , perfluoroalkyl, CO_2H , CO_2CH_3 , CONH_2 , CH_2OH , and vinyl groups. Side-reactions involving some of these functional groups were consistent with intermediates proposed in our earlier publications and begin to define the scope of this method for building chemical structures at interfaces.

- Reaction of Dichloromethane with Pyridine Derivatives under Ambient Conditions
Rudine, A. B.; Walter, M. G.; Wamser, C. C. *J. Org. Chem.* **2010**, 75, 4292–4295.

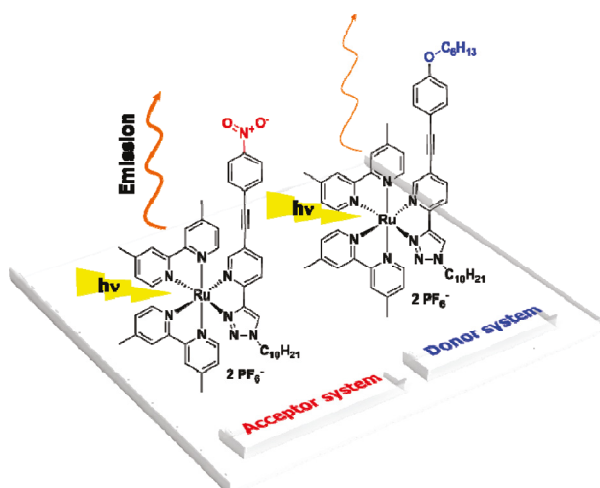
Abstract:



Pyridine derivatives and dichloromethane (DCM) are commonly used together in a variety of different applications. However, DCM slowly reacts with pyridine and a variety of other representative pyridine derivatives to form methylenebispyridinium dichloride compounds under ambient conditions. The proposed mechanism (two consecutive $\text{S}_{\text{N}}2$ reactions) was studied by evaluating the kinetics of the reaction between 4-(dimethylamino)pyridine and DCM. The second-order rate constants for the first (k_1) and second (k_2) substitutions were found to be $2.56(\pm 0.06) \times 10^{-8}$ and $4.29(\pm 0.01) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, respectively. Because the second substitution is so much faster than the first, the monosubstitution product could not be isolated or detected during the reaction; it was synthesized independently in order to observe its kinetics.

- N*-Heterocyclic Donor- and Acceptor-Type Ligands Based on 2-(1*H*-[1,2,3]Triazol-4-yl)pyridines and Their Ruthenium(II) Complexes
Happ, B.; Escudero, D.; Hager, M. D.; Friebe, C.; Winter, A.; Görls, H.; Altunta, E.; González, L.; Schubert, U. S. *J. Org. Chem.* **2010**, 75, 4025–4038.

Abstract:

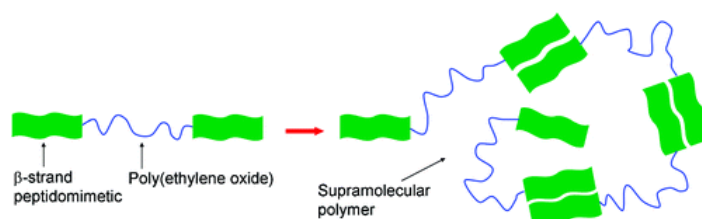


New 2-(1*H*-[1,2,3]triazol-4-yl)pyridine bidentate ligands were synthesized as bipyridine analogs, whereas different phenylacetylene moieties of donor and acceptor nature were attached at the 5-position of the pyridine unit. The latter moieties featured a crucial influence on the electronic properties of those ligands. The *N*-heterocyclic ligands were coordinated to ruthenium(II) metal ions by using a bis(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II) precursor. The donor or acceptor capability of the 2-(1*H*-[1,2,3]triazol-4-yl)pyridine ligands determined the quantum yield of the resulting ruthenium(II) complexes remarkably. Separately, 2-([1,2,3]triazol-4-yl)pyridine ligands are known to be potential quenchers, but using these new ligand systems led to room temperature emission of the corresponding ruthenium(II) complexes. The compounds have been fully characterized by elemental analysis, high-resolution ESI mass spectrometry, ^1H and ^{13}C NMR spectroscopy, and X-ray crystallography. Theoretical calculations for two ruthenium(II) complexes bearing a donor and acceptor unit, respectively, were performed to gain a deeper understanding of the photophysical behavior.

- Self-Assembly of Supramolecular Polymers from β -Strand Peptidomimetic–Poly(ethylene oxide) Hybrids

Isimjan, T. T.; de Bruyn, J. R.; Gillies, E. R. *Macromolecules* 2010, 43, 4453–4459.

Abstract:

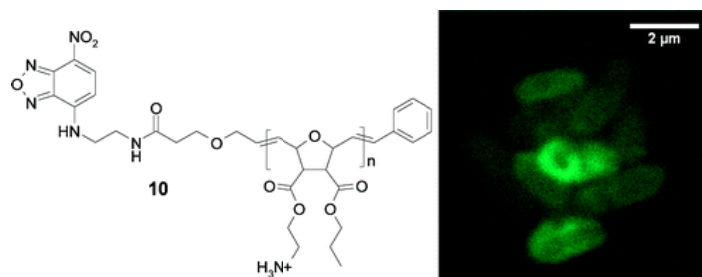


The use of hydrogen-bonding β -strand peptidomimetics for the preparation of supramolecular polymers is described here. The β -strand mimics were selected for their ability to form hydrogen bonds on only one face of the strand, allowing for controlled assembly into linear polymers. Alkyne-functionalized peptidomimetics with the capacity to form either four, six, or eight self-complementary hydrogen bonds were synthesized and conjugated to both termini of low molecular weight (MW) α,ω -diazidopoly(ethylene glycol). The assembly of these polymers into higher MW supramolecular polymers was investigated by multiangle light scattering, dynamic light scattering, and circular dichroism. It was found that the eight-hydrogen-bonding system was required for the significant formation of high MW assemblies and that the degree of assembly was dependent on the polymer concentration as well as the solvent. Thus, these peptidomimetics provide a new platform for the development of supramolecular polymers with the promise to tune their properties using functionalities on the amino acid side chains.

- End-Functionalized ROMP Polymers for Biomedical Applications

Madkour, A. E.; Koch, E. H. R.; Lienkamp, K.; Tew, G. N. *Macromolecules* 2010, 43, 4557–4561.

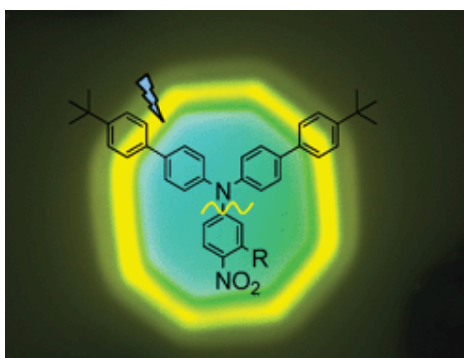
Abstract:



We present two novel allyl-based terminating agents that can be used to end-functionalize living polymer chains obtained by ring-opening metathesis polymerization (ROMP) using Grubbs' third generation catalyst. Both terminating agents can be easily synthesized and yield ROMP polymers with stable, storable activated ester groups at the chain end. These end-functionalized ROMP polymers are attractive building blocks for advanced polymeric materials, especially in the biomedical field. Dye labeling and surface coupling of antimicrobially active polymers using these end-groups were demonstrated.

- Tunable emissive thin films through ICT photodisruption of nitro-substituted triarylamines
Jacquart, A.; Tauc, P.; Pansu, R. B.; Ishow, E. *Chem. Commun.* **2010**, 46, 4360 – 4362.

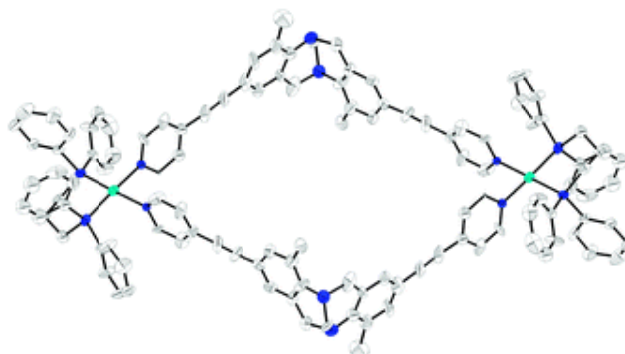
Abstract:



UV-assisted photocleavage in the solid state of orange emitting nitro-substituted triarylamines leads to the appearance of blue emission following photodisruption of the ICT state.

- Formation of an heterochiral supramolecular cage by diastereomer self-discrimination: fluorescence enhancement and C₆₀ sensing
Arribas, C. L.; Wendt, O. F.; Sundin, A. P.; Carling, C. J.; Wang, R.; Lemieux, R. P.; Wärnmark, K. *Chem. Commun.* **2010**, 46, 4381 – 4383.

Abstract:



Diastereomer discrimination was observed in the formation of a metallomacrocyclic cage from a racemic ligand based on Tröger's base. The metallomacrocyclic cage exhibited a dramatic increase in fluorescence

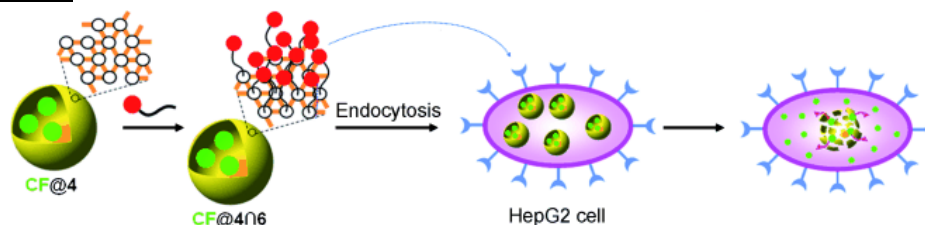
intensity compared to the ligand and its fluorescence was efficiently quenched by C₆₀.

9

- Facile, Template-Free Synthesis of Stimuli-Responsive Polymer Nanocapsules for Targeted Drug Delivery

Kim, E.; Kim, D.; Jung, H.; Lee, J.; Paul, S.; Selvapalam, N.; Yang, Y.; Lim, N.; Park, C. G.; Kim, K. *Angew. Chem. Int. Ed.* **2010**, 49, 4405–4408.

Abstract:

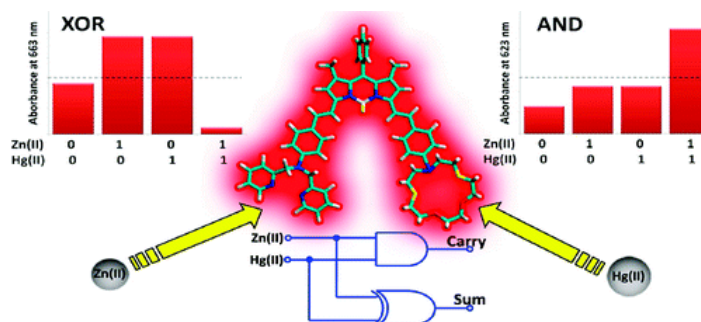


Open Sesame! A synthetic approach to stimuli-responsive polymer nanocapsules has been developed. The reductively labile polymer nanocapsule allows for not only facile, noncovalent surface modification but also the release of encapsulated cargo in response to a predefined redox stimulus in an intracellular environment.

- Selective Manipulation of ICT and PET Processes in Styryl-Bodipy Derivatives: Applications in Molecular Logic and Fluorescence Sensing of Metal Ions

Bozdemir, O. A.; Guliyev, R.; Buyukcakir, O.; Selcuk, S.; Kolenen, S.; Gulseren, G.; Nalbantoglu, T.; Boyaci, H.; U. Akkaya, E. *J. Am. Chem. Soc.* **2010**, 132, 8029–8036.

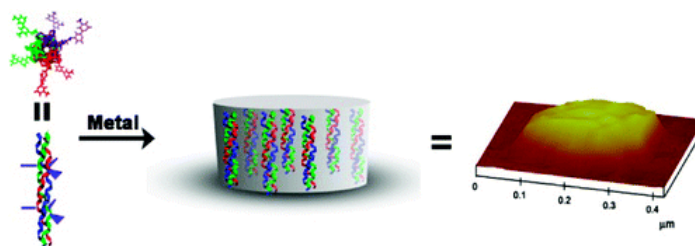
Abstract:



Remarkably versatile chemistry of Bodipy dyes allows the design and straightforward synthesis of multivalent-multitopic derivatives, which, with judicious selection of metal ion–ligand pairs based on known affinities, affords control and manipulation of photoinduced electron transfer and internal charge transfer processes as desired. We have demonstrated that metal ions acting as modulators (or inputs, in digital design parlance) can generate absorbance changes in accordance with the operation of a half-adder. In addition, an AND logic gate in the emission mode was delivered using a different binucleating arrangement of ligands. A molecular equivalent of a three-input AND logic gate was also obtained exploiting differential binding affinities of metal ions for different ligands. The results suggest that different metal ions can be used as nonannihilating inputs, selectively targeting various ligands incorporated within a single fluorophore, and with careful design, diverse photophysical processes can be selectively modulated, resulting in a range of signals, useful in molecular logic design, and offering an enticing potential for multianalyte chemosensors.

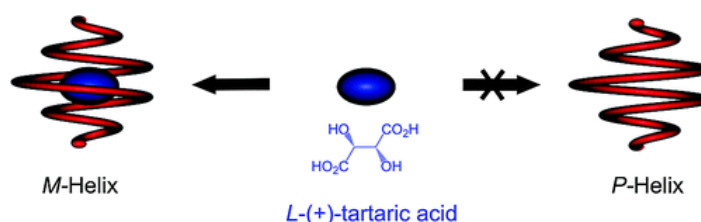
- Metal-Triggered Collagen Peptide Disk Formation

Przybyla, D. E.; Chmielewski, J. *J. Am. Chem. Soc.* **2010**, 132, 7866–7867.

Abstract:

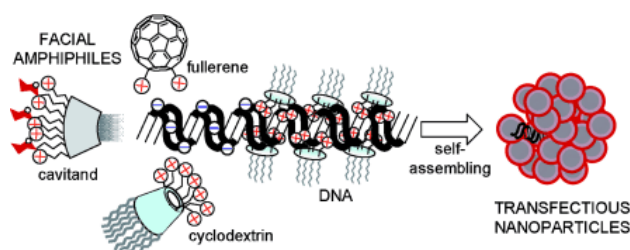
A collagen peptide was designed for metal-triggered, hierarchical assembly through a radial growth mechanism. To achieve radial assembly, H-(byp)₂ containing Pro-Hyp-Gly repeating sequences and two staggered bipyridine ligands within the peptide was synthesized. Triple helix formation resulted in the placement of six bipyridine ligands along the triple helix, and the addition of metal ions resulted in the formation of nanometer-sized collagen peptide disks. These structures were found to disassemble upon the addition of EDTA, demonstrating that radial assembly of collagen peptide triple helices could be realized with the addition of metal ions.

- Diastereoselective Encapsulation of Tartaric Acid by a Helical Aromatic Oligoamide
Ferrand, Y.; Kendhale, A. M.; Kauffmann, B.; Grélard, A.; Marie, C.; Blot, V.; Pipelier, M.; Dubreuil, D.; Huc, I. *J. Am. Chem. Soc.* **2010**, *132*, 7858–7859.

Abstract:

A helical aromatic oligoamide foldamer encapsulates tartaric acid with exceptional affinity, selectivity, and diastereoselectivity. The structure of the complex has been elucidated both in solution by NMR spectroscopy and in the solid state by X-ray crystallography, making it possible to rationalize the strong effects observed, particularly the role of hydrogen bonds between the hydroxyl and carboxylic acid groups of tartaric acid and the inner wall of the helically folded capsule, which completely surrounds the guest and insulates it from the solvent.

- Preorganized, Macromolecular, Gene-Delivery Systems
Ortiz Mellet, C.; Benito, J. M.; García Fernández, J. M. *Chem. Eur. J.* **2010**, *16*, 6728-6742.

Abstract:

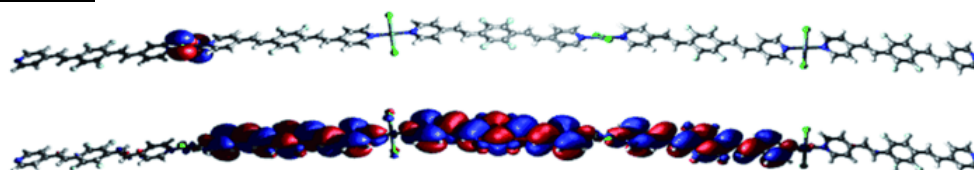
Viruses represent a paradigmatic example of multicomponent, self-organized supramolecular systems specialized in the delivery and replication of their genetic material. Mimicking their functioning by artificial synthetic molecules represents a fantastic challenge that will lead to the future development of gene therapy. This is only possible if general approaches towards the construction of nanoscale vehicles for DNA are developed and the key rules governing their capacity

to compact genetic material and its active transport/delivery through cell membranes are understood. In this area of research, synthetic organic chemistry plays an important role by providing tools to create tailor-made molecules of increasing complexity. Preorganization of functional elements onto macromolecular platforms has the potential to allow control of the self-assembling behavior of discrete architectures to produce nanometric objects that can be programmed to complex, compact, deliver, and release plasmid DNA in a target cell.

- Designing Surface-Confined Coordination Oligomers

Altman, M.; Rachamim, M.; Ichiki, T.; Iron, M. A.; Evmenenko, G.; Dutta, P.; van der Boom, M. E. *Chem. Eur. J.* **2010**, *16*, 6744-6747.

Abstract:



Designer materials: HOMO-LUMO engineering of coordination-based oligomers covalently bound to silicon or glass has been achieved by the use of a partially fluorinated chromophore (see graphic). The experimental and computationally derived physical chemical properties of these assemblies are compared to their non-fluorinated analogues.