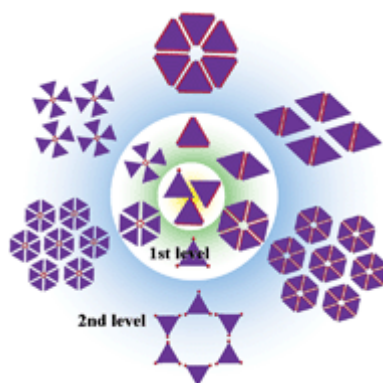


- Hierarchical construction of self-assembled low-dimensional molecular architectures observed by using scanning tunneling microscopy

1

Yang, Y.; Wang, C. *Chem. Soc. Rev.* **2009**, *38*, 2576 – 2589.

Abstract:

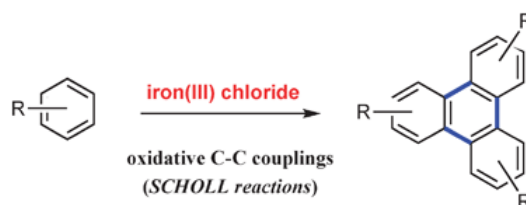


This *tutorial review* is intended to reflect the progress in constructing functional low-dimensional molecular nanostructures on surfaces through hierarchical self-assembly processes. Hierarchical assembly can be characterized as a multilevel process, and represented by categories depending on symmetry characteristics and the nature of intermolecular interactions. Various approaches have been explored in order to gain knowledge on tailoring hierarchical assembly characteristics, driving mechanisms and designing principles. The advances in hierarchical assembly structures could benefit the efforts towards constructing well-defined molecular architectures, which are important to the development of novel material properties and molecular devices.

- Iron(III) chloride in oxidative C–C coupling reactions

Sarhan, A. A. O.; Bolm, C. *Chem. Soc. Rev.* **2009**, *38*, 2730 – 2744.

Abstract:



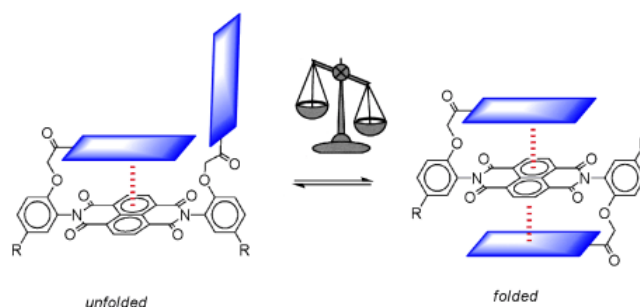
Simple iron(III) chloride is an excellent reagent for the oxidative formation of new C-C-bonds.

In this *critical review*, the use of iron(III) chloride in oxidative C–C couplings of arenes and related unsaturated compounds is presented and reviewed. The approach allows highly selective dimerisations of phenol derivatives, naphthols, and heterocyclic compounds. Sequential couplings give access to structurally well-defined oligo- and polymers. Iron(III) chloride is commercially available and inexpensive. Being a mild oxidising agent it has been applied in numerous reactions leading to new carbon—carbon-bonds in complex molecular arrays (107 references).

- A High-Barrier Molecular Balance for Studying Face-to-Face Arene-Arene Interactions in the Solid State and in Solution

Chong, Y. S.; Carroll, W. R.; Burns, W. G.; Smith, M. D.; Shimizu, K. D. *Chem. Eur. J.* **2009**, *15*, 9117 – 9126.

Abstract:

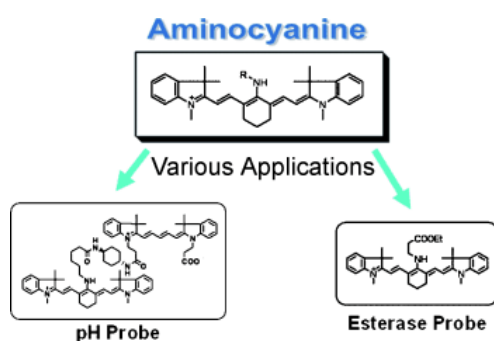


Keep the balance! A versatile molecular balance was developed to study face-to-face arene-arene interactions (see scheme). The *anti/syn* ratio yields a measure of the strength of the intramolecular interactions in solution. X-ray structure analysis of the *anti* isomers characterized the orientation and distances of the interactions in the solid state.

- Molecular Design Strategies for Near-Infrared Ratiometric Fluorescent Probes Based on the Unique Spectral Properties of Aminocyanines

Kiyose, K.; Aizawa, S.; Sasaki, E.; Kojima, H.; Hanaoka, K.; Terai, T.; Urano, Y.; Nagano, T. *Chem. Eur. J.* **2009**, *15*, 9191 – 9200.

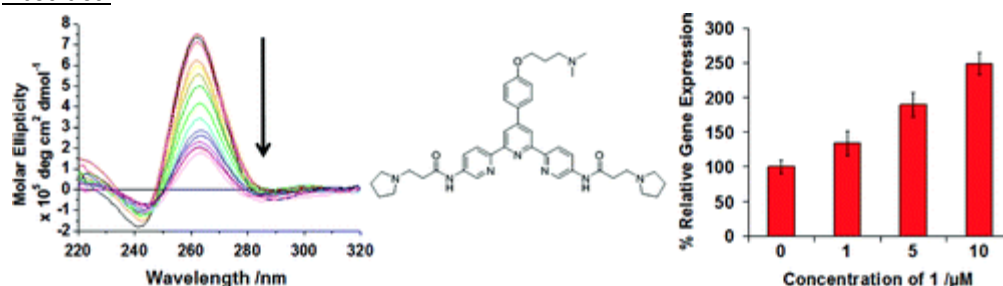
Abstract:



Probing for information: Amine-substituted tricarbocyanines have unique spectral properties on which two strategies for the development of near-infrared (NIR) ratiometric fluorescent probes are based. These approaches were validated by obtaining tricarbocyanine-based ratiometric NIR fluorescent probes for esterase and for pH level (see scheme).

- A Small Molecule That Disrupts G-Quadruplex DNA Structure and Enhances Gene Expression

Abstract:

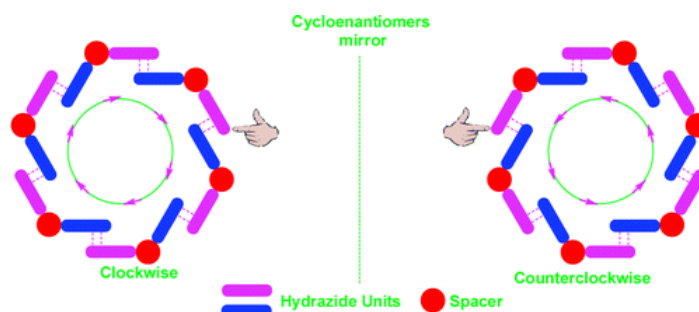


It has been hypothesized that the formation of G-quadruplex structures in the DNA of gene promoters may be functionally linked to transcription and consequently that small molecules that interact with such G-quadruplexes may modulate transcription. We previously reported that triarylpyridines are a class of small molecules that selectively interact with G-quadruplex DNA. Here

we describe an unexpected property of one such ligand that was found to disrupt the structure of two different DNA G-quadruplex structures, each derived from sequence motifs in the promoter of the proto-oncogene *c-kit*. Furthermore, cell-based experiments in a cell line that expresses *c-kit* (HGC-27) showed that the same ligand increased the expression of *c-kit*. This contrasts with G-quadruplex-inducing ligands that have been previously found to inhibit gene expression. It would thus appear that the functional consequence of small molecule ligands interacting with G-quadruplex structures may depend on the specific mode of interaction. These observations provide further evidence to suggest that G-quadruplex forming sequence motifs play a role that relates to transcription.

- Noncovalent Synthesis of Shape-Persistent Cyclic Hexamers from Ditopic Hydrazide-Based Supramolecular Synthons and Asymmetric Induction of Supramolecular Chirality  
Yang, Y.; Xue, M.; Xiang, J.; Chen, C. J. *Am. Chem. Soc.* **2009**, *131*, 12657–12663.

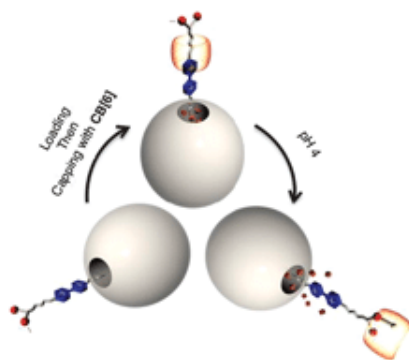
Abstract:



With properly encoded recognition sites and a well-defined algorithm for intermolecular and intramolecular interactions, the 120° spacer linked ditopic hydrazide-based supramolecular synthons were found to self-assemble into shape-persistent cyclic hexamers in apolar solvents. The two hydrazide motifs displayed separate sets of signals in the NMR spectra because of the interlocked conformation. While in hydrogen bonding competitive solvent such as DMSO-*d*<sub>6</sub> the spectra were in agreement with the structures with C<sub>2</sub> axes. Moreover, the terminative groups were found to affect the stability of the assemblies substantially. Consequently, the monomer with ureido-hydrazide terminative groups could form the most stable cyclic hexamer in solution for the attractive spectator secondary electrostatic interactions. Owing to the dynamically and kinetically stable nature of these kinds of assemblies, the assembly from the monomer with chiral auxiliary terminative groups also displayed supramolecular chirality in solution, which was confirmed by concentration-dependent CD spectra.

- pH-Responsive mechanised nanoparticles gated by semirotaxanes.  
Khashab, N. M.; Belowich, M. E.; Trabolsi, A.; Friedman, D. C.; Valente, C.; Lau, Y.; Khatib, H. A.; Zink, J. I.; Stoddart, J. F. *Chem. Commun.* **2009**, 5371 – 5373.

Abstract :

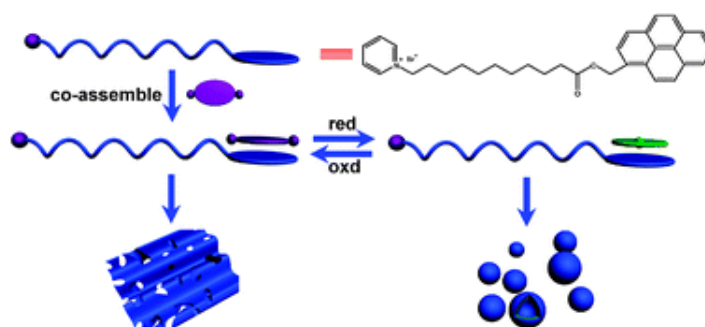


A [2]pseudorotaxane-based mechanised nanoparticle system, which operates within an aqueous acidic environment, has been prepared and characterised; this integrated system affords both water-soluble stalk and ring components in an effort to improve the biocompatibility of these promising new drug delivery vehicles.

- Redox responsive supramolecular amphiphiles based on reversible charge transfer interactions.

Wang, C.; Guo, Y.; Wang, Y.; Xu, H.; Zhang, X. *Chem. Commun.* **2009**, 5380 – 5382.

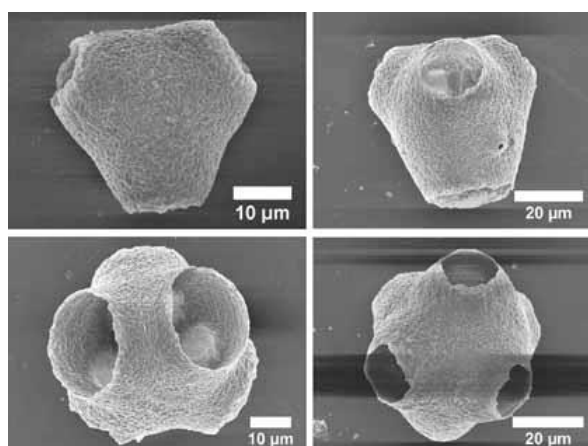
Abstract :



We have fabricated a charge transfer interaction driven supramolecular amphiphile, the self-assembly nanostructures of which can change between vesicles and irregular continuous aggregates reversibly in response to redox stimuli.

- Nonspherical Colloidosomes with Multiple Compartments from Double Emulsions  
Lee, D.; Weitz, D. A. *Small* **2009**, 5, 1932-1935.

Abstract:



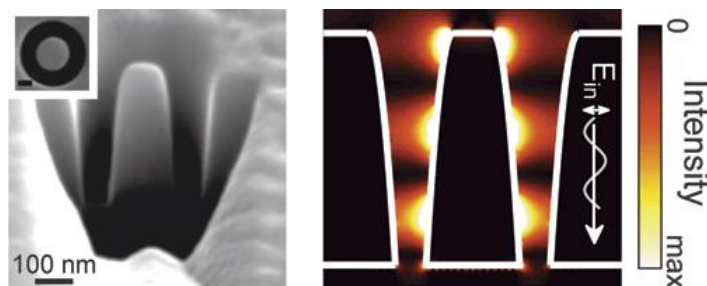
Nonspherical colloidosomes with multiple compartments are generated using water-in-oil-in-water double emulsions with controlled morphology as templates (see image). Double emulsions are

prepared using a glass capillary microfluidic device that provides a precise means to control the number of internal aqueous droplets and the volume ratio of oil and aqueous phases

- Plasmon Dispersion in Coaxial Waveguides from Single-Cavity Optical Transmission Measurements

de Waele, R.; Burgos, S. P.; Polman, A.; Atwater, H. A. *Nano Lett.* **2009**, *9*, 2832–2837.

Abstract:

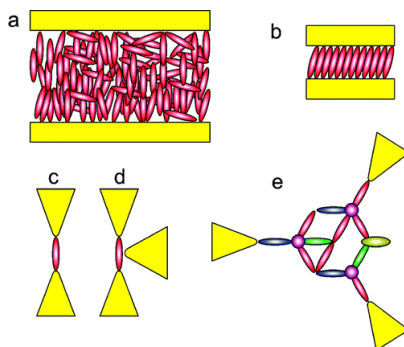


We determine the plasmon dispersion relation in coaxial waveguides composed of a circular channel separating a metallic core and cladding. Optical transmission measurements are performed on isolated coaxial nanoapertures fabricated on a Ag film using focused ion-beam lithography. The dispersion depends strongly on the dielectric material and layer thickness. Our experimental results agree well with an analytical model for plasmon dispersion in coaxial waveguides. We observe large phase shifts at reflection from the end facets of the coaxial cavity, which strongly affect the waveguide resonances and can be tuned by changing the coax geometry, composition, and surrounding dielectric index, enabling coaxial cavities with ultrasmall mode volumes.

- Digital Information Processing in Molecular Systems

Szaciłowski, K. *Chem. Rev.* **2008**, *108*, 3481-3548.

Abstract:



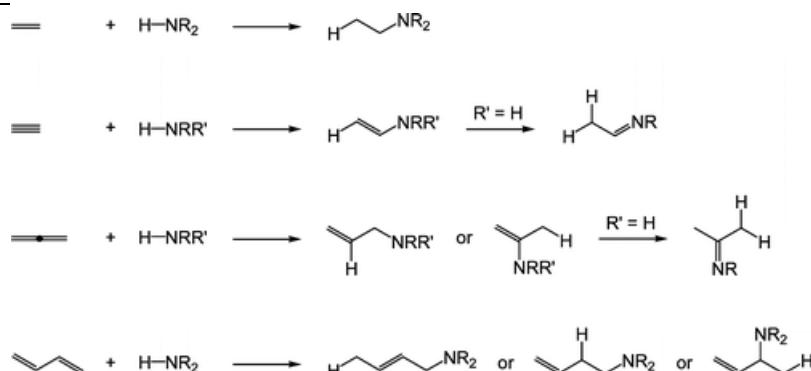
Digital electronics is so widely used in everyday life that it is almost impossible to find an electric device that does not make use of digital electronic components. On average, 85% of the circuitry in all the electronic devices is digital and only 15% is analog. Due to the ease of construction, resistance to interference, and low cost, more and more electronic systems become digitalized. In digital systems, information is contained in series of zeros and ones, represented usually as low and high voltages, while in analog systems, the whole continuum of states must be considered. Therefore, in contrast to analog systems, information processing in digital systems is straightforward and based on very simple principles of Boolean logic (vide infra). Digital systems are much less sensitive to any interference due to wide margins of allowed signal values resulting in turn from highly nonlinear characteristics. Any real digital device is characterized by signal rise time and signal fall time. These

times limit the rate of information processing, as the pulse duration (time required for one binary operation) cannot be shorter than the rise (or fall) time.

- Hydroamination: Direct Addition of Amines to Alkenes and Alkynes

Mller, T. E.; Hultsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795-3892.

Abstract:



Nitrogen-containing compounds, such as amines, enamines, and imines, are valuable and commercially important bulk chemicals, specialty chemicals, and pharmaceuticals. Among various synthesis routes, hydroamination, the direct formation of a new C–N bond by addition of an amine to an unsaturated CC bond, is of particular significance. The reaction offers an atom-efficient pathway starting from readily accessible alkenes and alkynes. While the reaction is thermodynamically feasible under normal conditions (slightly exothermic but nearly ergoneutral, because hydroamination reactions are entropically negative, in particular in the intermolecular variant), there is a high reaction barrier. The 2 + 2 cycloaddition of N–H across the CC bond, which is orbital-forbidden under thermal conditions but can be promoted with light, can be avoided by the use of a catalyst opening other reaction pathways. However, relatively low reaction temperatures (generally ≤200–300 °C) are required, because the conversion is limited by the reaction equilibrium at higher temperatures.

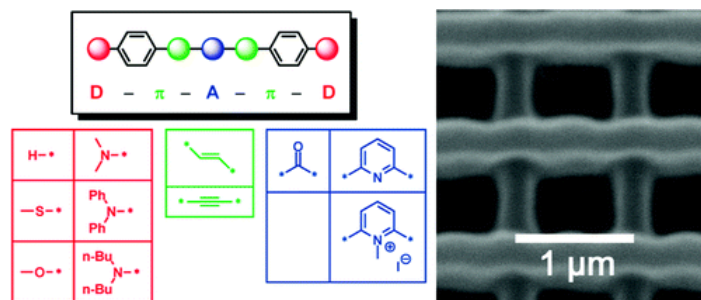
The hydroamination of alkenes is more difficult compared with that of alkynes because of the lower reactivity and electron density of C=C bonds. A particular challenge is the reversal of the regiochemistry to obtain the anti-Markovnikov product. For good reason, the catalytic anti-Markovnikov addition of H–NR<sub>2</sub> to olefins was listed as one of the so-called “Ten Challenges for Catalysis”. During recent years, hydroamination became a widely explored operation in the synthesis of nitrogen heterocycles and complex molecules. The Markovnikov addition of protected amines to alkynes is now an established synthesis strategy. With the development of a new generation of catalysts, the addition of protected amines to alkenes will quickly become a routine reaction. More challenging and, thus, demanding further development time is the conversion of strongly basic amines, such as ammonia, as well as achieving adequate control of the regioselectivity in anti-Markovnikov fashion.

- Structure-Activity Relationship in D-π-A-π-D-Based Photoinitiators for the Two-Photon-Induced Photopolymerization Process.

Pucher, N.; Rosspointner, A.; Satzinger, V.; Schmidt, V.; Gescheidt, G.; Stampfl, J.; Liska, R. *Macromolecules* **2009**, *42*, 6519–6528.

Abstract:



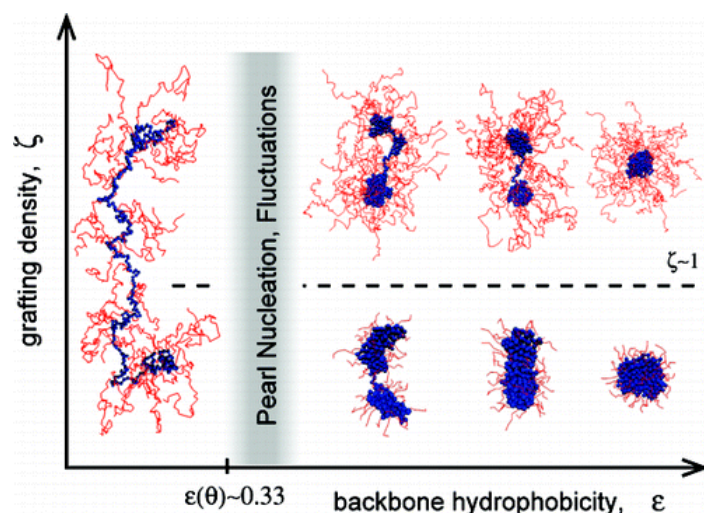


This article presents the synthesis and characterization of a series of cross-conjugated D- $\pi$ -A- $\pi$ -D-based photoinitiators for the two-photon-induced photopolymerization process. Different donor and acceptor functionalities and derivatives containing double and triple bonds in the conjugated backbone allowed the evaluation of structure-activity relationship. Investigation of the basic photophysical properties showed high extinction coefficients at around 400 nm and none or vanishingly small emission quantum yields. The evaluated initiators showed at least similar activity, and in some cases broader processing windows than well-known highly active initiators from the literature and by far better results than commercially available initiators in terms of two-photon-induced microfabrication. These results are well in accordance with the TPA cross section values for the compounds measured by z-scan analysis. By using optimized parameters, structures with line widths of about 250 nm were obtained at photoinitiator concentrations as low as 0.05 wt %.

- Amphiphilic Graft Copolymers in Selective Solvents: Molecular Dynamics Simulations and Scaling Theory.

Košovan, P.; Kuldová, J.; Limpouchová, Z.; Procházka, K.; Zhulina, E. B.; Borisov, O. V. *Macromolecules* **2009**, *42*, 6748–6760.

Abstract:



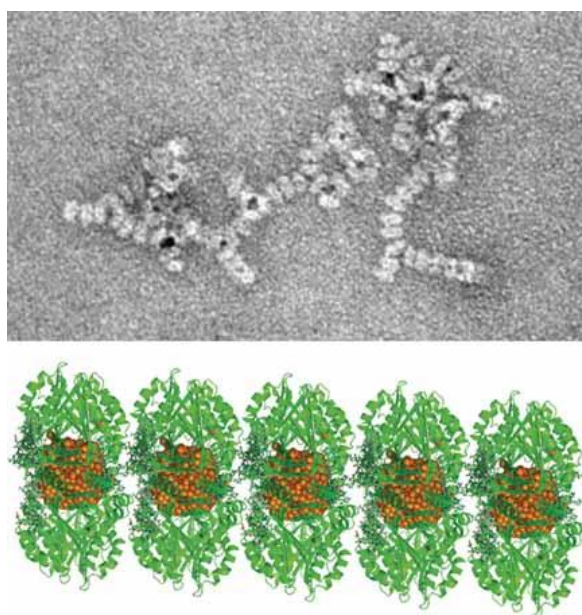
Intramolecular structures in amphiphilic graft copolymers with hydrophilic side chains and hydrophobic backbone have been studied by molecular dynamics simulations. In accordance with earlier theoretical predictions [Borisov, O.; Zhulina, E. *Macromolecules* **2005**, *38*, 2506-2514], we have found that balance of repulsive and attractive intramolecular interactions may result in the pearl-necklace-type conformations. The globular “pearls” are formed by collapsed segments of the main chain comprising multiple spacers; these pearls are stabilized against aggregation by repulsive interactions of the hydrophilic grafts. The size of the pearls is controlled by the intramolecular hydrophilic-hydrophobic balance, whereas the total number of pearls in the graft copolymer depends

on the length of the main chain. For graft copolymer with relatively long spacers we have observed intramolecular conformational transition from pearl-necklace structure to unimolecular cylindrical micelle upon a decrease in the solvent quality for the main chain. The results of simulations, in particular behavior of polymers of finite chain length, are rationalized on the basis of revised and extended scaling theory.

- Constrained Synthesis and Organization of Catalytically Active Metal Nanoparticles by Self-Assembled Protein Templates

Behrens, S.; Heyman, A.; Maul, R.; Essig, S.; Steigerwald, S.; Quintilla, A.; Wenzel, W.; Bürck, J.; Dgany, O.; Shoseyov, O. *Adv. Mater.* **2009**, 3515-3519.

Abstract:

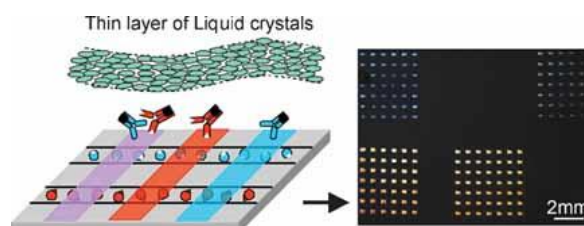


Novel geometrical architectures of hybrid nanoparticle-protein complexes are generated by chemically synthesizing monodisperse metal nanoparticles in situ in the presence of a stable, stress-related protein. The catalytic activity of the protein-particle hybrids is examined for the reduction of 4-nitrophenol, providing future biofunctional nanoparticle labels for catalytic signal amplification in optical assays.

- Exploring Optical Properties of Liquid Crystals for Developing Label-Free and High-Throughput Microfluidic Immunoassays

Xue, C.-Y.; Khan, S. A.; Yang, K.-L. *Adv. Mater.* **2009**, 198-202.

Abstract:



The orientational transition of liquid crystals (LCs) is used as a label-free detection mechanism for immunoassays developed in microfluidic systems. LCs only show bright optical textures (visible to the naked eye) in the line-line intersections in which label-free antibodies bind to their surface-

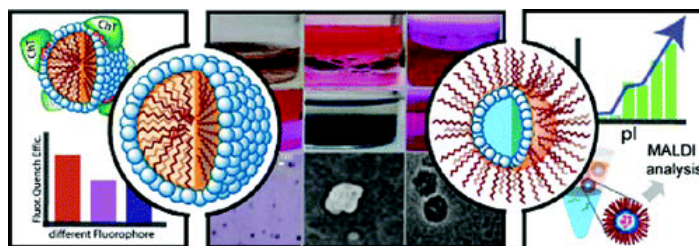


immobilized antigens, suggesting the feasibility of using LCs to detect specific antigen-antibody binding events in a high-throughput and multiplexed manner.

- Supramolecular Assemblies of Amphiphilic Homopolymers

Kale, T. S.; Klaikherd, A.; Popere, B.; Thayumanavan, S. *Langmuir* **2009**, *25*, 9660–9670.

Abstract:

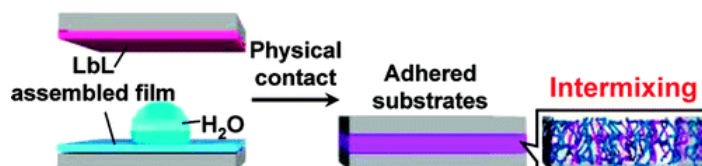


Amphiphilic molecules self-assemble in solvents because of the differential solvation of the hydrophilic and lipophilic functionalities. Small-molecule surfactants have long been known to form micelles in water that can solubilize lipophilic guest molecules in their water-excluded interior. Polymeric surfactants based on block copolymers are also known to form several types of aggregates in water owing either to the mutual incompatibility of the blocks or better solvation of one of the blocks by the solvent. Incorporating amphiphilicity at smaller length scales in polymers would provide an avenue to capture the interesting properties of macromolecules and fine tune their supramolecular assemblies. To address this issue, we designed and synthesized amphiphilic homopolymers containing hydrophilic and lipophilic functionalities in the monomer. Such a polymer can be imagined to be a string of small-molecule surfactants tethered together such that the hydrophilic and lipophilic functionalities are located on opposite faces, rendering the assemblies facially amphiphilic. This feature article describes the self-assembly of our amphiphilic homopolymers in polar and apolar solvents. These homopolymers not only form micelles in water but also form inverse micelles in organic solvents. Subtle changes to the molecular structure have been demonstrated to yield vesicles in water and inverted micelles in organic solvents. The characterization of these assemblies and their applications in separations, catalysis, and sensing are described here.

- Adhesion of Two Physically Contacting Planar Substrates Coated with Layer-by-Layer Assembled Films

Matsukuma, D.; Aoyagi, T.; Serizawa, T. *Langmuir* **2009**, *25*, 9824–9830.

Abstract:



Adhesives composed of synthetic and low-cost molecules that are based on simple chemical principles are attractive because of their versatility. In this article, we report adhesion between two planar substrates coated with layer-by-layer (LbL) assembled films of cationic poly(diallyldimethylammonium chloride) (PDDA) and anionic poly(sodium styrenesulfonate) (PSS) and perform lap shear measurements of the adhered substrates. Films prepared on the substrates functioned as adhesives when one substrate coated with the PDDA-surface film contacted the other surface coated with the PSS-surface film under adequate pressure in the presence of water droplets,

suggesting that two films adhered on the basis of polyion complex formation. Observations suggested that the adhesives failed at the substrate-film interface rather than at the bulk films. The adhesion was compared between film-coated substrates and noncoated ones. Confocal laser scanning microscopic observation of adhesives composed of fluorescently labeled poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) revealed that the labeled PAH assembled on one substrate was well dispersed, even in a nonlabeled film assembled on another substrate. It was therefore confirmed that after adhesion in the presence of the water component, the polyelectrolytes became intermixed between the glassy films, resulting in changes in the adhesive structure at the substrate-film interface.