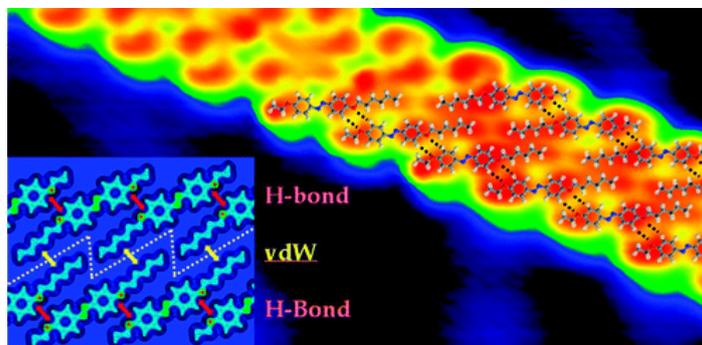


- Switchable Supramolecular Polymers from the Self-Assembly of a Small Monomer with Two Orthogonal Binding Interactions

Kim, H. W.; Jung, J.; Han, M.; Lim, S.; Tamada, K.; Hara, M.; Kawai, M.; Kim, Y.; Kuk, Y. *J. Am. Chem. Soc.* **2011**, *133*, 9236-9238.

Abstract:

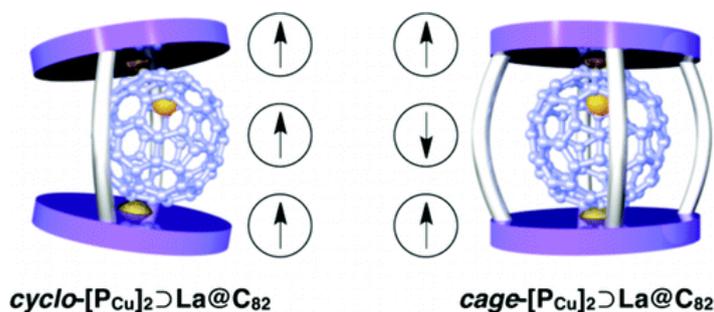


We synthesized an azobenzene derivative to demonstrate a one-dimensional molecular zipper. The formation and underlying mechanism of the molecular zipper formed by combined hydrogen-bonding and van der Waals interactions between adjacent molecules were investigated on a Au(111) surface using scanning tunneling microscopy and density functional theory calculations.

- Ferromagnetic Spin Coupling between Endohedral Metallofullerene La@C₈₂ and a Cyclodimeric Copper Porphyrin upon Inclusion

Hajjaj, F.; Tashiro, K.; Nikawa, H.; Mizorogi, N.; Akasaka, T.; Nagase, S.; Furukawa, K.; Kato, T.; Aida, T. *J. Am. Chem. Soc.* **2011**, *133*, 9290-9292.

Abstract:

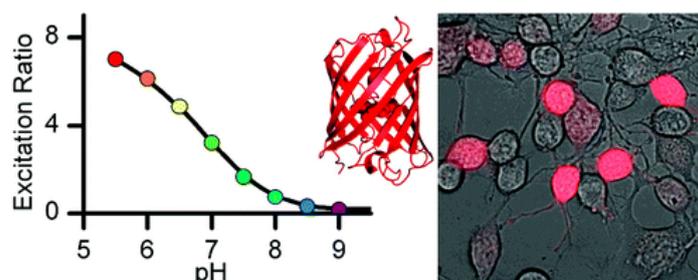


The cyclic host *cyclo*-[P_{Cu}]₂ carrying two covalently connected Cu(II) porphyrin units can accommodate La@C₈₂, a paramagnetic endohedral metallofullerene, in its cavity to form the inclusion complex *cyclo*-[P_{Cu}]₂⊃La@C₈₂, which can be transformed into the caged complex *cage*-[P_{Cu}]₂⊃La@C₈₂ by ring-closing olefin metathesis of its side-chain olefinic termini. On the basis of electron spin resonance (ESR) and electron spin transient nutation (ESTN) studies, *cyclo*-[P_{Cu}]₂⊃La@C₈₂ is the first ferromagnetically coupled inclusion complex featuring La@C₈₂, whereas *cage*-[P_{Cu}]₂⊃La@C₈₂ is ferrimagnetic.

- Imaging Intracellular pH in Live Cells with a Genetically Encoded Red Fluorescent Protein Sensor

Tantama, M.; Hung, Y. P.; Yellen, G. *J. Am. Chem. Soc.* **2011**, *133*, 10034-10037.

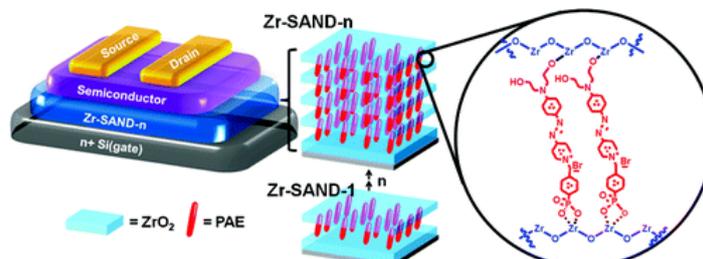
Abstract:



Intracellular pH affects protein structure and function, and proton gradients underlie the function of organelles such as lysosomes and mitochondria. We engineered a genetically encoded pH sensor by mutagenesis of the red fluorescent protein mKeima, providing a new tool to image intracellular pH in live cells. This sensor, named pHRed, is the first ratiometric, single-protein red fluorescent sensor of pH. Fluorescence emission of pHRed peaks at 610 nm while exhibiting dual excitation peaks at 440 and 585 nm that can be used for ratiometric imaging. The intensity ratio responds with an apparent pK_a of 6.6 and a >10-fold dynamic range. Furthermore, pHRed has a pH-responsive fluorescence lifetime that changes by ~ 0.4 ns over physiological pH values and can be monitored with single-wavelength two-photon excitation. After characterizing the sensor, we tested pHRed's ability to monitor intracellular pH by imaging energy-dependent changes in cytosolic and mitochondrial pH.

- Solution-Deposited Organic–Inorganic Hybrid Multilayer Gate Dielectrics. Design, Synthesis, Microstructures, and Electrical Properties with Thin-Film Transistors
Ha, Y.; Emery, J. D.; Bedzyk, M. J.; Usta, H.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 10239–10250.

Abstract:

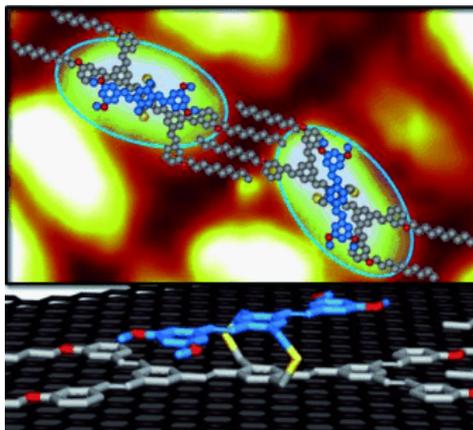


We report here on the rational synthesis, processing, and dielectric properties of novel layer-by-layer organic/inorganic hybrid multilayer dielectric films enabled by polarizable π -electron phosphonic acid building blocks and ultrathin ZrO_2 layers. These new zirconia-based self-assembled nanodielectric (Zr-SAND) films (5–12 nm thick) are readily fabricated via solution processes under ambient atmosphere. Attractive Zr-SAND properties include amenability to accurate control of film thickness, large-area uniformity, well-defined nanostructure, exceptionally large electrical capacitance (up to 750 nF/cm^2), excellent insulating properties (leakage current densities as low as 10^{-7} A/cm^2), and excellent thermal stability. Thin-film transistors (TFTs) fabricated with pentacene and PDIF-CN₂ as representative organic semiconductors and zinc–tin–oxide (Zn–Sn–O) as a representative inorganic semiconductor function well at low voltages ($< \pm 4.0 \text{ V}$). Furthermore, the TFT performance parameters of representative organic semiconductors deposited on Zr-SAND films, functionalized on the surface with various alkylphosphonic acid self-assembled monolayers, are investigated and shown to correlate closely with the alkylphosphonic acid chain dimensions.

- Janus-Like 3D Tectons: Self-Assembled 2D Arrays of Functional Units at a Defined Distance from the Substrate

Bléger, D.; Mathevet, F.; Kreher, D.; Attias, A.-J.; Bocheux, A.; Latil, S.; Douillard, L.; Fiorini-Debuisschert, C.; Charra, F. *Angew. Chem. Int. Ed.* **2011**, *50*, 6562–6566.

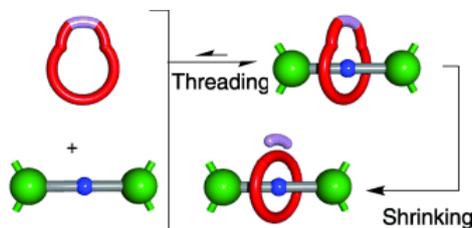
Abstract:



Janus faces: The Janus-like 3D tecton is a doubly functionalized molecular building block that consists of two different faces (see picture, gray: A and blue: B) linked by a rigid spacer. A is designed to act as a pedestal capable of guiding 2D self-assembly on the substrate, while B is a functional entity. This versatile approach allows for the creation of periodic arrays of functional units at a defined distance from the conductive substrate.

- A Metal-Free “Threading-Followed-by-Shrinking” Protocol for Rotaxane Synthesis
Hsueh, S.-Y.; Ko, J.-L.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Angew. Chem. Int. Ed.* **2011**, *50*, 6643–6646.

Abstract:

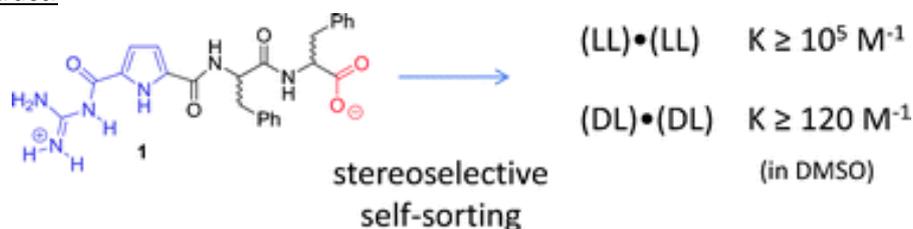


Shrinking ring size: Synthesis of a [2]rotaxane has employed photoextrusion of SO₂ from the arylmethyl sulfone motif of a [2]pseudorotaxane. A dumbbell-shaped guest molecule allows a shrinking reaction to decrease the number of atoms in the ring skeleton of the macrocyclic component of the [2]pseudorotaxane (see picture).

- Stereoselective self-sorting in the self-assembly of a Phe–Phe extended guanidiniocarbonyl pyrrole carboxylate zwitterion: formation of two diastereomeric dimers with significantly different stabilities

Rodler, F.; Sicking, W.; Schmuck, C. *Chem. Commun.* **2011**, *47*, 7953-7955.

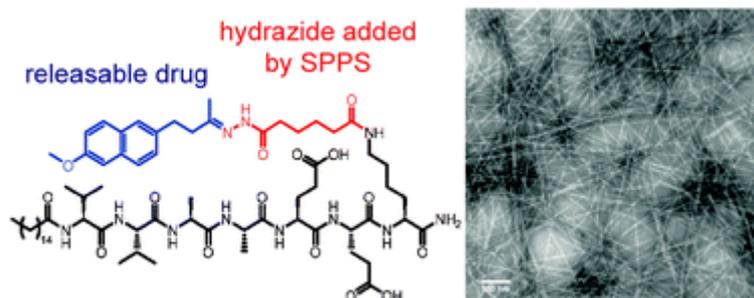
Abstract:



In a highly stereoselective self-sorting process the different stereoisomers of zwitterion 1 self-assemble exclusively into homochiral dimers.

- Drug release from hydrazone-containing peptide amphiphiles
Matson, J. B.; Stupp, S. I. *Chem. Commun.* **2011**, 47, 7962-7964.

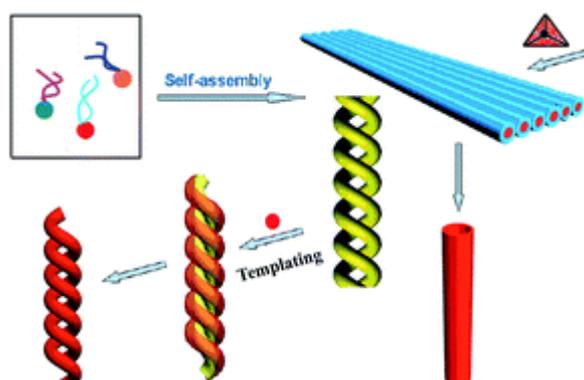
Abstract:



Hydrazone-containing peptide amphiphiles were investigated as drug-releasing peptide nanofiber gels using nabumetone as a model drug.

- Construction and application of tunable one-dimensional soft supramolecular assemblies
Yan, Y.; Lin, Y.; Qiao, Y.; Huang, J. *Soft Matter* **2011**, 7, 6385-6398.

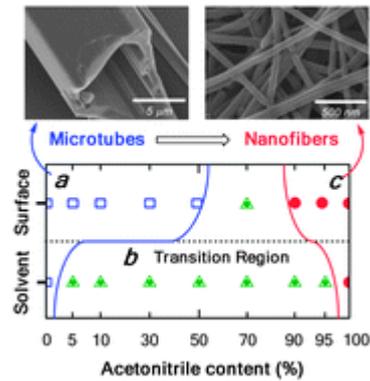
Abstract:



Self-assembly of small molecules into one-dimensional soft nanostructures offers many advantages in understanding biological process and fabrication of electronically active materials. In recent decades, various one-dimensional soft nanostructures have been fabricated. The present review focuses on the following content: (1) frequently occurring forces in one-dimensional molecular self-assembly; (2) how these forces are used to construct this type of nanostructures; (3) fine-tuning one-dimensional self-assemblies by employing tools such as photo, pH, temperature, additives, and concentration; (4) some examples of the applications of one-dimensional self-assemblies in fabrication of one-dimensional hard materials are described.

- Solvent and surface controlled self-assembly of diphenylalanine peptide: from microtubes to nanofibers
Huang, R.; Qi, W.; Su, R.; Zhao, J.; He, Z. *Soft Matter* **2011**, 7, 6418-6421.

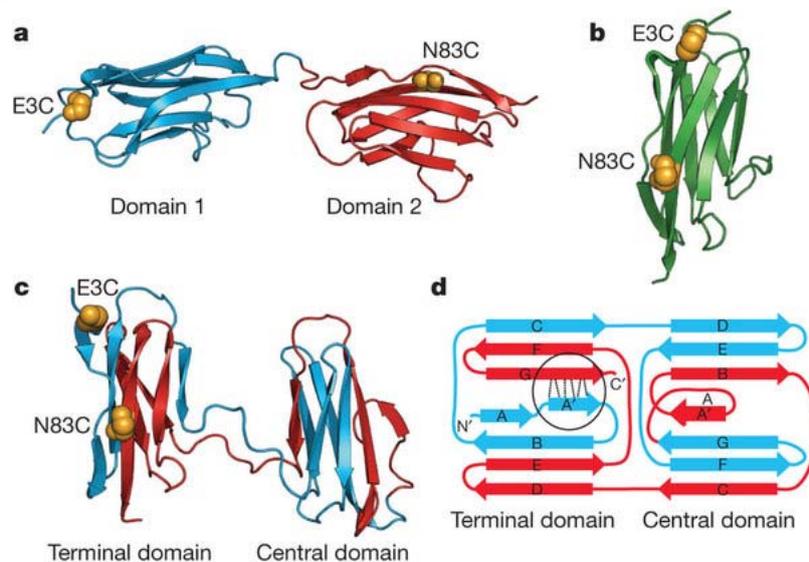
Abstract:



A new approach based on solvent and surface effects was developed for controlling the self-assembly of diphenylalanine peptide into microtubes and nanofibers. The HBD/HBA ability and surface tension may be major determinants in the formation of these peptide assemblies. Our results will lead to a better understanding of the molecular mechanisms involved in diphenylalanine self-assembly process.

- Single-molecule fluorescence reveals equencespecific misfolding in multidomain proteins
Borgia, M. B.; Borgia, A.; Best, R. B.; Steward, A.; Nettels, D.; Wunderlich, B.; Schuler, B.; Clarke, J. *Nature*, **2011**, 474, 662-666.

Abstract:

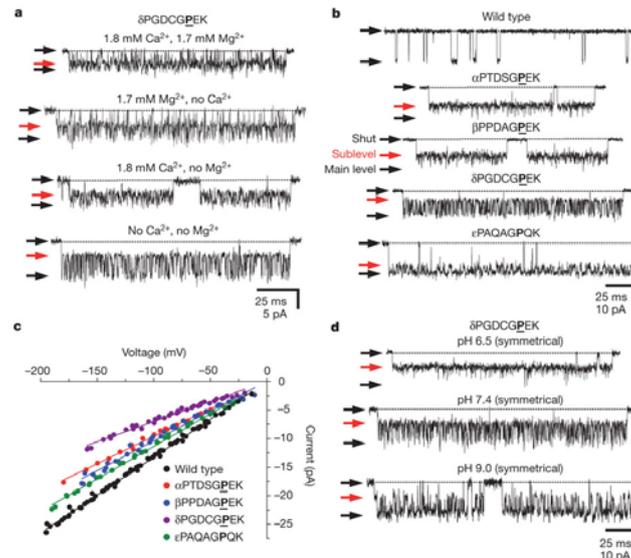


A large range of debilitating medical conditions is linked to protein misfolding, which may compete with productive folding particularly in proteins containing multiple domains. Seventy-five per cent of the eukaryotic proteome consists of multidomain proteins, yet it is not understood how interdomain misfolding is avoided. It has been proposed that maintaining low sequence identity between covalently linked domains is a mechanism to avoid misfolding. Here we use single-molecule Förster resonance energy transfer to detect and quantify rare misfolding events in tandem immunoglobulin domains from the I band of titin under native conditions. About 5.5 per cent of molecules with identical domains misfold during refolding in vitro and form an unexpectedly stable state with an unfolding half-time of several days. Tandem arrays of immunoglobulin-like domains in humans show significantly lower sequence identity between neighbouring domains than between non-adjacent domains. In particular, the sequence identity of neighbouring domains has been found to be preferentially below 40 per cent. We observe no misfolding for a tandem of naturally neighbouring

domains with low sequence identity (24 per cent), whereas misfolding occurs between domains that are 42 per cent identical. Coarse-grained molecular simulations predict the formation of domain-swapped structures that are in excellent agreement with the observed transfer efficiency of the misfolded species. We infer that the interactions underlying misfolding are very specific and result in a sequence-specific domain-swapping mechanism. Diversifying the sequence between neighbouring domains seems to be a successful evolutionary strategy to avoid misfolding in multidomain proteins.

- Tunable pKa values and the basis of opposite charge selectivities in nicotinic-type receptors
Cymes, G. D.; Grosman, C. *Nature* **2011**, *474*, 526-531.

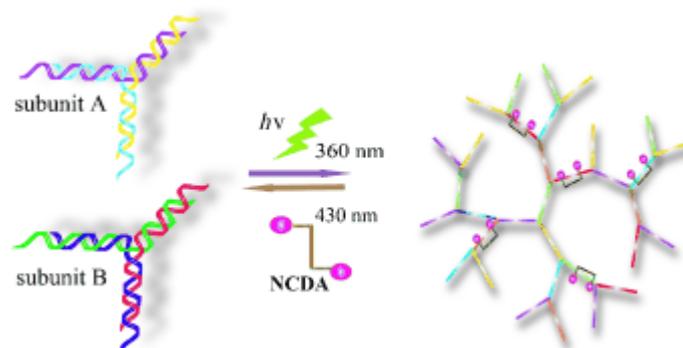
Abstract:



Among ion channels, only the nicotinic-receptor superfamily has evolved to generate both cation- and anion-selective members. Although other, structurally unrelated, neurotransmitter-gated cation channels exist, no other type of neurotransmitter-gated anion channel, and thus no other source of fast synaptic inhibitory signals, has been described so far. In addition to the seemingly straight forward electrostatic effect of the presence (in the cation selective members) or absence (in the anion-selective ones) of a ring of pore-facing carboxylates, mutational studies have identified other features of the amino-acid sequence near the intracellular end of the pore-lining transmembrane segments (M2) that are also required to achieve the high charge selectivity shown by native channels. However, the mechanism underlying this more subtle effect has remained elusive and a subject of speculation. Here we show, using single-channel electrophysiological recordings to estimate the protonation state of native ionizable side chains, that anion-selective-type sequences favour whereas cation-selective type sequences prevent the protonation of the conserved, buried basic residues at the intracellular entrance of the pore (the M2 09 position). We conclude that the previously unrecognized tunable charge state of the 09 ring of buried basic side chains is an essential feature of these channels' versatile charge-selectivity filter.

- Molecular-Glue-Triggered DNA Assembly To Form a Robust and Photoresponsive Nano-Network
Wang, C.; Pu, F.; Lin, Y.; Ren, J.; Dohn, C.; Nakatani, K.; Qu, X. *Chem. Eur. J.* **2011**, *17*, 8189-8194.

Abstract:

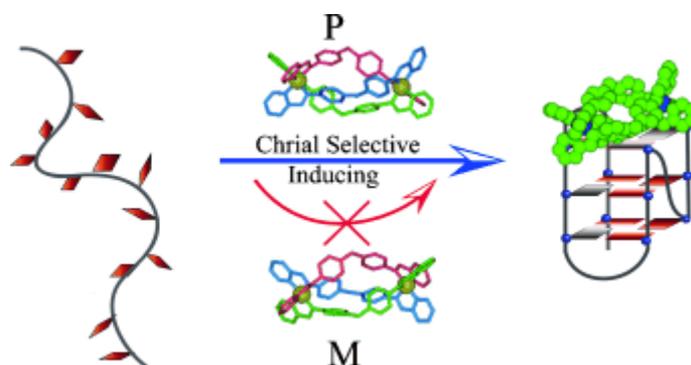


A robust and photoresponsive DNA network has been designed and constructed from branched DNA and molecular glue. The molecular glue is photoswitchable and can specifically bind to G–G mismatched double-stranded DNA. The assembly process can be reversibly controlled by manipulating the wavelength of light. The approach is flexible, allowing tuning of the size, morphology as well as the cavity of the network by variation of the molar ratio and the isotropic/anisotropic character of the branched building blocks. The assembled architectures are versatile and heat tolerant. These properties should allow the use of the network in further applications.

- Chiral Metallo–Supramolecular Complexes Selectively Induce Human Telomeric G-Quadruplex Formation under Salt-Deficient Conditions

Zhao, C.; Geng, J.; Feng, L.; Ren, J.; Qu, X. *Chem. Eur. J.* **2011**, *17*, 8209-8215.

Abstract:

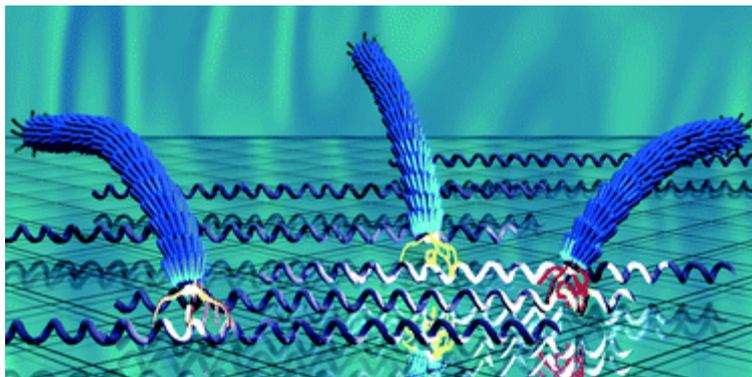


Chiral molecular recognition of human telomeric DNA is important for rational drug design and developing structural probes of G-quadruplexes. Here we report that a chiral supramolecular complex can selectively induce human telomeric G-quadruplex formation and discriminate different G-quadruplex sequences under salt-deficient conditions studied by circular dichroism (CD), UV meltings, stopped-flow spectroscopy, fluorescence resonance energy transfer, enzyme cleavage, and gel electrophoresis. P-enantiomer induced G-quadruplex formation is fast and does not require a large excess of P enantiomer. More importantly, this chiral compound induces loop sequence-dependent G-quadruplex formation.

- Specific interfaces between synthetic polymers and biologically identified peptides

Serizawa, T.; Matsuno, H.; Sawada, T. *J. Mater. Chem.* **2011**, *21*, 10252-10260.

Abstract:

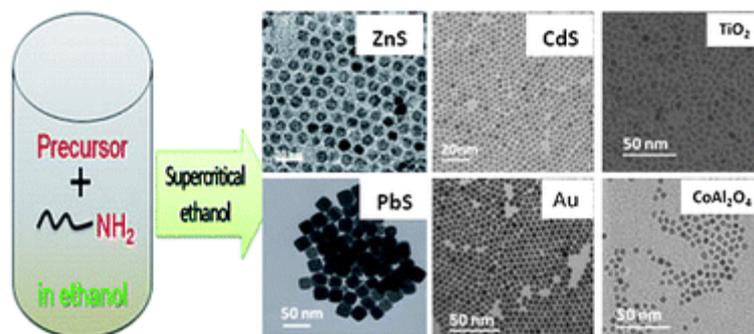


Investigations into the interfaces between synthetic polymers and biomolecules are important in the biomedical materials field. Over the past decade, combinatorial biotechnologies such as the phage display and cell-surface display methods, in which random peptide libraries are displayed on phage bodies and cell surfaces, have been utilized to identify oligopeptides that specifically recognize the surfaces of artificial materials. The resulting peptides were chemically and biotechnologically utilized as novel functional nanomaterials. In this article, our recent progress in the identification and applications of polymer-binding peptides is reviewed. We show that various nanostructures of synthetic polymers can be the specific targets of biologically identified peptides, and that the peptides can be utilized in polymer science and technology.

- Synthesis of monodispersed nanocrystalline materials in supercritical ethanol: a generalized approach

Pahari, S. K.; Adschiri, T.; Panda, A. *J. Mater. Chem.* **2011**, *21*, 10377-10383.

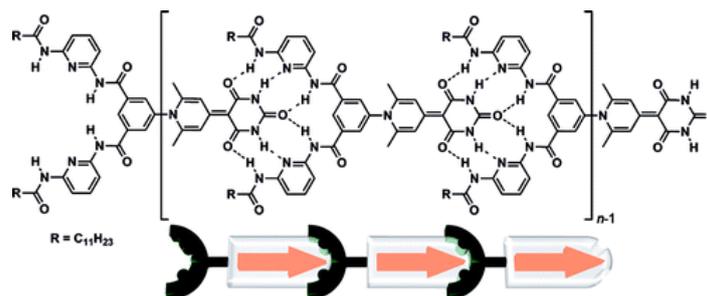
Abstract:



We report a generalized approach for synthesis of a variety of nearly monodisperse inorganic nanostructured materials with different sizes and shapes using supercritical ethanol (SCE). In the present synthetic strategy the inorganic precursor and stabilizer (long chain amines) were co-solubilised in ethanol. Decomposition of the precursor occurred under supercritical conditions and facilitated rapid homogeneous nucleation, growth, and crystallization of the desired nanoparticles in near monodisperse state. The size and shape of the synthesized nanoparticles were tuned by varying the synthetic parameters. The particles exhibited size- and shape-dependent properties, and could be readily dispersed in hexane and toluene. Controlled evaporation of solvent from the dispersions yielded fairly ordered 2D structures.

- Hydrogen-Bond-Directed Formation of Supramolecular Polymers Incorporating Head-to-Tail Oriented Dipolar Merocyanine Dyes

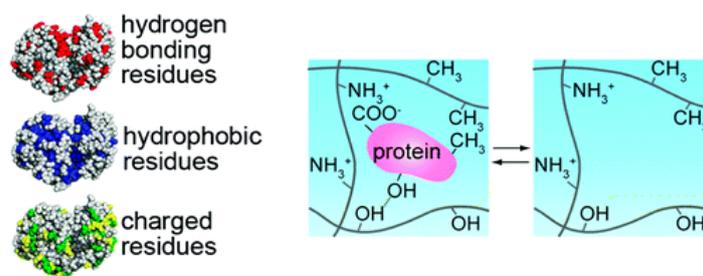
Schmidt, R.; Stolte, M.; Grüne, M.; Würthner, F. *Macromolecules* **2011**, *44*, 3766–3776.

Abstract:

A self-complementary Hamilton-receptor-functionalized merocyanine dye has been synthesized by incorporating a hydrogen bonding receptor site to the donor moiety of a merocyanine chromophore that bears a barbituric acid acceptor unit. The optical and electro-optical properties of monomeric dyes have been studied by UV-vis, fluorescence, and electro-optical absorption spectroscopy in chloroform, 1,4-dioxane, tetrahydrofuran, and dimethyl sulfoxide under dilute condition. The self-assembly properties of this self-complementary merocyanine in solution have been investigated by concentration- and temperature-dependent UV-vis and one- and two-dimensional NMR spectroscopy. These studies revealed that the present merocyanine dyes self-assemble in a head-to-tail fashion by forming six hydrogen bonds. The size of the assemblies in solution was determined by dynamic light scattering and diffusion-ordered spectroscopy NMR investigations. In nonpolar solvent mixtures at high concentrations, this merocyanine dye forms appreciably fluorescent gels ($\Phi_{fl} = 0.17$) while the monomeric dye and self-assemblies in solution are only weakly fluorescent ($\Phi_{fl} = 0.07$).

- Molecular Imprinting of Maltose Binding Protein: Tuning Protein Recognition at the Molecular Level

Zayats, M.; Kanwar, M.; Ostermeier, M.; Searson, P. C. *Macromolecules* **2011**, *44*, 3966–3972.

Abstract:

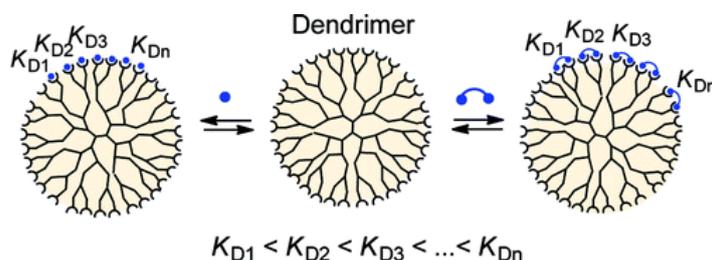
Protein imprinting in hydrogels is one approach for developing artificial receptors capable of specific recognition and binding of a target molecule. Through selection of monomers with side groups that can interact with the target protein and control over the degree of cross-linking, the architecture and spatial distribution of interaction points can be optimized for a target protein. Here we report on the imprinting of polyacrylamide-based hydrogels with maltose binding protein (MBP). To design the optimum architecture, we analyze the distribution of surface amino acid residues on the protein surface. We show that the selectivity of MBP recognition is increased by incorporating monomers that can introduce sites for hydrogen bonding, hydrophilic interactions, and electrostatic interactions. MBP-imprinted films showed high specificity and could discriminate between reference proteins with similar molecular weight, dimensions, and isoelectric point.

- Specificity and Negative Cooperativity in Dendrimer–Oxime Drug Complexation

Choi, S. K.; Leroueil, P.; Li, M.-H.; Desai, A.; Zong, H.; Van Der Spek, A. F. L.; Baker, Jr., J. R. *Macromolecules* **2011**, *44*, 4026–4029.

10

Abstract:

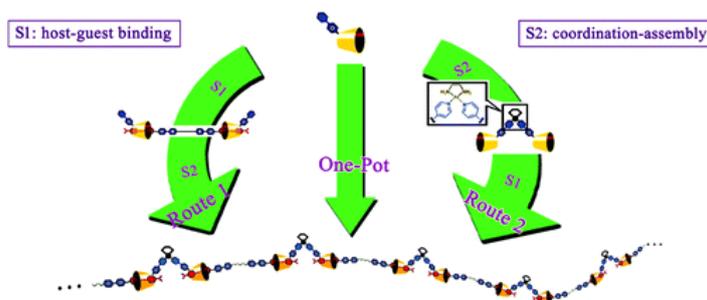


Dendrimers are a family of nanometer-sized, spherical macromolecules that have inspired a multitude of chemical, biological, and biomedical applications. In particular, poly(amidoamine) (PAMAM) dendrimers have a well-defined core–shell architecture characterized by repetitive cavities and branches suitable for guest molecule complexation. Therefore, PAMAM dendrimers have been frequently used to make complexes with small molecule drugs, oligonucleotides, and genetic therapeutics for drug delivery and gene transfer applications. Despite many extensive demonstrations of this approach to therapeutics, very few studies provide analysis of the molecular interaction between the dendrimer and the guest molecule in the nanoscale architecture. We report here binding analysis and molecular models that are of fundamental importance to understanding such processes. Using oxime-based guest molecules, we discuss evidence that the individual binding events contributing to the complexation at a global level occur in a specific and negatively cooperative manner.

- Construction of Polypseudorotaxane from Low-Molecular Weight Monomers via Dual Noncovalent Interactions

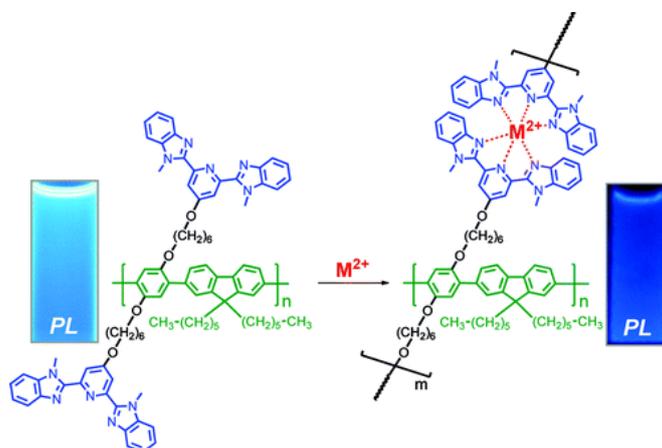
Zhu, L.; Lu, M.; Zhang, Q.; Qu, D.; Tian, H. *Macromolecules* **2011**, *44*, 4092–4097.

Abstract:



The design and construction of polypseudorotaxanes via noncovalent interactions from low-molecular weight monomers (LMWMs) is playing an important role in the field of supramolecular polymers. In this work, we synthesized three low-molecular weight compounds for supramolecular polymerizations and attempted to employ the metal–ligand interaction between the pyridine nitrogen and Pd (II), for cooperating with the host–guest binding between azobenzene and β -cyclodextrin (β -CD), to complete the end-to-end connection of the polymer chains. Routes for stepwise introduction of two of the self-assembly behaviors as well as a one-pot preparation were investigated by ^1H NMR and 2D nuclear Overhauser enhancement spectroscopy (NOESY) ^1H NMR spectroscopy. The self-assembly strategies based on the full orthogonality of both noncovalent interactions will allow for a smart and rapid synthesis of precise structural controlled supramolecular polymeric assemblies.

- Conjugated Polymer with Benzimidazolypyridine Ligands in the Side Chain: Metal Ion Coordination and Coordinative Self-Assembly into Fluorescent Ultrathin Films
Welterlich, I.; Tieke, B. *Macromolecules* **2011**, *44*, 4194–4203.

Abstract:

The synthesis and characteristic properties of a new conjugated copolymer with poly(phenylene-*alt*-fluorene) main chain and 2,6-bis(1'-methylbenzimidazolyl)pyridine (bip) ligands attached to the main chain via flexible spacer groups are described. The copolymer was prepared upon Pd-catalyzed Suzuki coupling of the 2,7-bis(pinacolatoboron) ester of 9,9-dihexylfluorene and a 1,4-dibromobenzene derivative carrying two ω -bip-substituted alkoxy groups in the 2- and 5-position. The yield was 88%. The polymer is readily soluble in common organic solvents and exhibits a strong blue fluorescence with maximum at 416 nm; the fluorescence quantum yield in toluene is 85%. UV/vis titration of the polymer with zinc chloride in toluene/methanol (99:1 v/v) and ferrous perchlorate in toluene/methanol (24:1 v/v) indicates formation of 2:1 ligand:metal ion (bis)complexes. Complex formation is accompanied by ion specific color changes (ionochromism) and quenching of the ligand fluorescence. The backbone fluorescence is partially retained. The coordinative interactions between the ligand-substituted polymer ("polytopic ligand") and the divalent metal ions (Zn(II), Cu(II)) can be used for layer-by-layer assembly of organized films on solid supports. Multiple sequential adsorption of metal salts and polymer leads to coordinative supramolecular assembly of the cross-linked polymer–metal ion complex on the substrate, the thickness being controlled by the number of adsorption steps applied. Since the fluorescence of the polymer backbone is not completely quenched by the ligand–metal ion interaction, the films exhibit a bluish luminescence. The new materials might be useful for metal ion sensing and for preparation of fluorescent coatings.