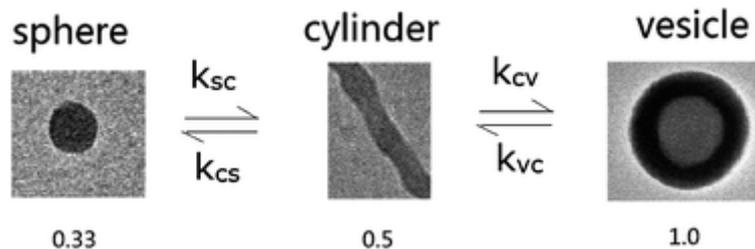


- Hydrogen bonding effect on micellization and morphological transformations of the polystyrene-block-poly(ethylene oxide) micelles  
Wang, C.; Yang, S.; Yu, X.; Zheng, J. X.; Ma, J.; Xu, J.; Zhu, M. *Soft Matter* **2012**, *8*, 10307-10313.

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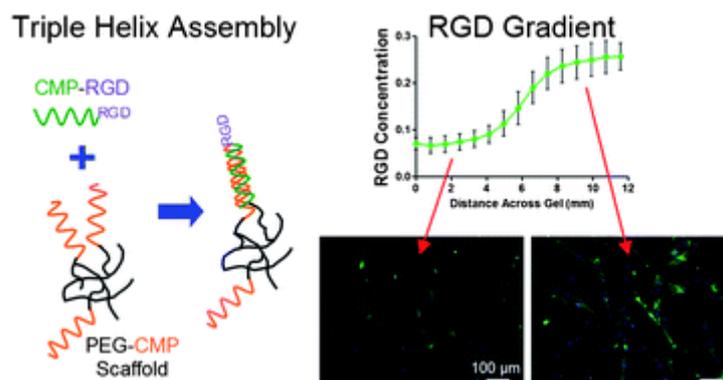
Abstract:



Diblock copolymer polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) forms micelles in a mixed solvent of *N,N*-dimethylformamide (DMF)–water. Poly(acrylic acid) (PAA) and poly(methyl acrylic acid) (PMAA) were introduced to the solution in order to study the effect of hydrogen bonding (H-bonding) complexation on the micellization process. The H-bonding complexation changes the micellization free energy of PS-*b*-PEO, and more importantly affects the kinetics of the morphological transformation of the micelles with temperature, which provides helpful insights into the time-dependence of the isothermal relaxation process from non-equilibrium to equilibrium.

- Encoding cell-instructive cues to PEG-based hydrogels via triple helical peptide assembly  
Stahl, P. J.; Yu, S. M. *Soft Matter* **2012**, *8*, 10409-10418.

Abstract:

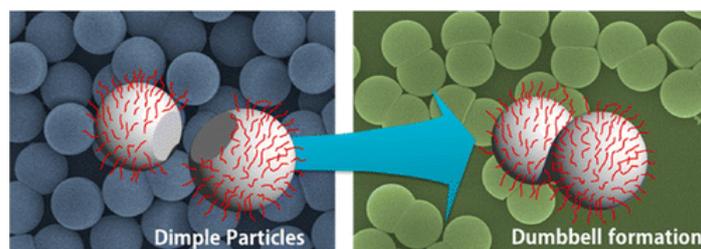


Effective synthetic tissue engineering scaffolds mimic the structure and composition of the natural extracellular matrix (ECM) to promote optimal cellular adhesion, proliferation, and differentiation. Among many proteins of the ECM, collagen and fibronectin are known to play a key role in the structural integrity of the scaffold as well as its ability to support cell adhesion. Here, we present photocrosslinked poly(ethylene glycol) diacrylate (PEGDA) hydrogels displaying collagen mimetic peptides (CMPs) that can be further conjugated to bioactive molecules *via* a CMP–CMP triple helix association. Pre-formed PEGDA–CMP hydrogels can be encoded with varying concentrations of cell-signaling CMP–RGD peptides similar to cell adhesive fibronectin decorating the collagen fibrous network by non-covalent binding. Furthermore, the triple helix mediated encoding allows facile generation of spatial gradients and patterns of cell-instructive cues across the cell scaffold that simulate the distribution of insoluble factors in the natural ECM.

- Synthesis and Assembly of Colloidal Particles with Sticky Dimples

Kim, S.-H.; Hollingsworth, A. D.; Sacanna, S.; Chang, S.-J.; Lee, G.; Pine, D. J.; Yi, G.-R. *J. Am. Chem. Soc.* **2012**, *134*, 16115–16118.

Abstract:

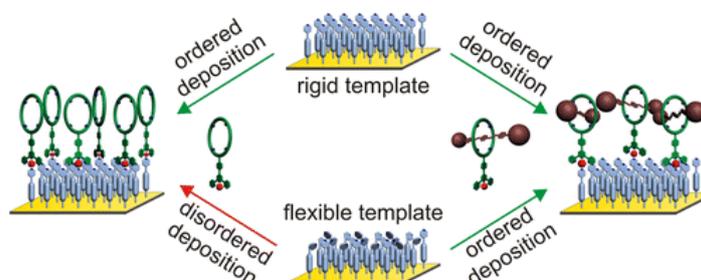


The preparation of anisotropic colloidal particles by a simple yet versatile temperature-controlled swelling process is described. The resulting polymeric particles feature a surface dimple, the size and shape of which were determined by the amount of oil captured in particles and the interfacial tension between the three phases: polystyrene (PS), decane, and the suspending medium. Following the removal of free or physically adsorbed surfactant from the swollen particles, hydrophobic dimples were produced upon evaporation of the oil phase. We demonstrate the spontaneous assembly of these ‘dimpled particles’ into dumbbell shapes or trimers through a site-selective hydrophobic interaction.

- Deposition of Ordered Layers of Tetralactam Macrocycles and Ether Rotaxanes on Pyridine-Terminated Self-Assembled Monolayers on Gold

Richter, S.; Poppenberg, J.; Traulsen, C. H.-H.; Darlatt, E.; Sokolowski, A.; Sattler, D.; Unger, W. E. S.; Schalley, C. A. *J. Am. Chem. Soc.* **2012**, *134*, 16289–16297.

Abstract:

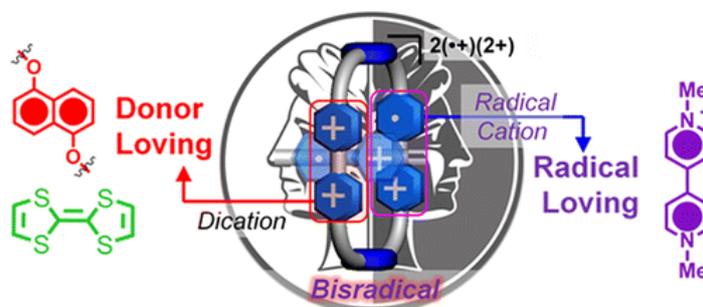


The deposition of tetralactam macrocycles and the corresponding benzyl ether rotaxanes on gold substrates is investigated for the first time exploiting metallo-supramolecular chemistry. Two pyridine-terminated self-assembled monolayers (SAMs) are developed that are used as well-ordered template layers. The two SAMs differ with respect to the rigidity of the terminal pyridines as shown by angle-resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The template layers are then used for the metal-mediated self-assembly of macrocycles and rotaxanes on solid supports. The SAM with the more rigid terminal pyridine shows a higher coverage with the macrocycles and is therefore preferable. Angle-resolved NEXAFS spectroscopy also shows the deposited supramolecules to be oriented preferentially upright. This order is only achieved for the macrocycles through the deposition on the more rigid SAM template, whereas rotaxanes form oriented layers on both SAMs. Time-of-flight secondary-ion mass spectrometry analysis was used to determine the deposition time required for the self-assembly process.

- Radically Enhanced Molecular Switches

Fahrenbach, A. C.; Zhu, Z.; Cao, D.; Liu, W.-G.; Li, H.; Dey, S. K.; Basu, S.; Trabolsi, A.; Botros, Y. Y.; Goddard, W. A.; Stoddart, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 16275–16288.

Abstract:

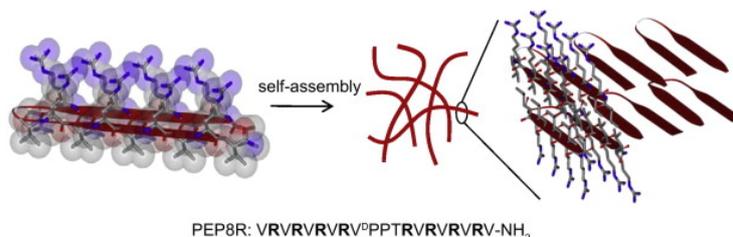


The mechanism governing the redox-stimulated switching behavior of a tristable [2]rotaxane consisting of a cyclobis(paraquat-p-phenylene) (CBPQT<sup>4+</sup>) ring encircling a dumbbell, containing tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) recognition units which are separated from each other along a polyether chain carrying 2,6-diisopropylphenyl stoppers by a 4,4'-bipyridinium (BIPY<sup>2+</sup>) unit, is described. The BIPY<sup>2+</sup> unit acts to increase the lifetime of the metastable state coconformation (MSCC) significantly by restricting the shuttling motion of the CBPQT<sup>4+</sup> ring to such an extent that the MSCC can be isolated in the solid state and is stable for weeks on end. As controls, the redox-induced mechanism of switching of two bistable [2]rotaxanes and one bistable [2]catenane composed of CBPQT<sup>4+</sup> rings encircling dumbbells or macrocyclic polyethers, respectively, that contain a BIPY<sup>2+</sup> unit with either a TTF or DNP unit, is investigated. Variable scan-rate cyclic voltammetry and digital simulations of the tristable and bistable [2]rotaxanes and [2]catenane reveal a mechanism which involves a bisradical state coconformation (BRCC) in which only one of the BIPY<sup>•+</sup> units in the CBPQT<sup>2(•+)</sup> ring is oxidized to the BIPY<sup>2+</sup> dication. This observation of the BRCC was further confirmed by theoretical calculations as well as by X-ray crystallography of the [2]catenane in its bisradical tetracationic redox state. It is evident that the incorporation of a kinetic barrier between the donor recognition units in the tristable [2]rotaxane can prolong the lifetime and stability of the MSCC, an observation which augurs well for the development of nonvolatile molecular flash memory devices.

- Arginine-rich self-assembling peptides as potent antibacterial gels

Veiga, A. S.; Sinthuvanich, C.; Gaspar, D.; Franquelim, H. G.; Castanho, M. A. R. B.; Schneider, J. P. *Biomaterials* **2012**, *33*, 8907-8916.

Abstract:



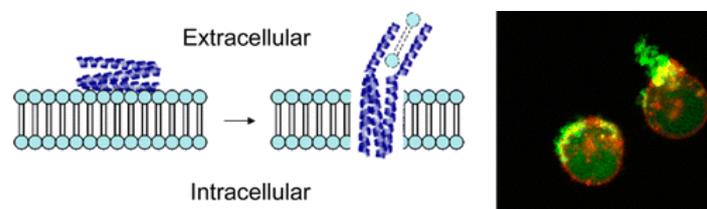
Hydrogel materials that display inherent activity against bacteria can be used to directly treat accessible wounds to prevent or kill existing infection. Hydrogels composed of self-assembling  $\beta$ -hairpin peptides, having a high content of arginine, were found to be extremely effective at killing both gram-positive and gram-negative bacteria, including multi-drug resistant *Pseudomonas*

*aeruginosa*. No added antibacterial agents are necessary to realize activity. Using self-assembling peptides for material construction allows facile structure–activity relationships to be determined since changes in peptide sequence at the monomer level are directly transposed to the bulk material's antibacterial properties. SAR studies show that arginine content largely influences the hydrogel's antibacterial activity, and influences their bulk rheological properties. These studies culminated in an optimized gel, composed of the peptide PEP6R (VKVRVRVRV<sup>D</sup>PPTRVRVRVKV). PEP6R gels prepared at 1.5 wt % or higher concentration, demonstrate high potency against bacteria, but are cytocompatible toward human erythrocytes as well as mammalian mesenchymal stem cells. Rheological studies indicate that the gel is moderately stiff and displays shear-thin recovery behavior, allowing its delivery via simple syringe.

- Peptide Self-Assembly on Cell Membranes to Induce Cell Lysis

Chen, L.; Patrone, N.; Liang, J. F. *Biomacromolecules* **2012**, *13*, 3327–3333.

Abstract:

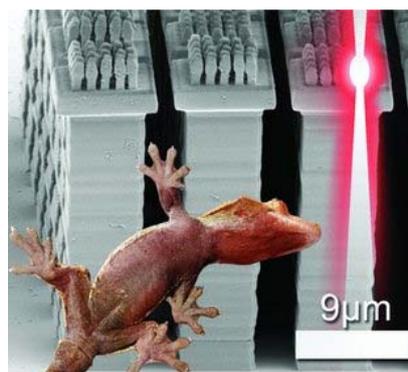


Self-assembling into aggregates with defined structures is a common phenomenon for many peptides at high concentrations. In this study, we found that when PTP-7b (FLGALFKALSHLL), a concentration-dependent self-assembling peptide, bound to tissue cells and accumulated on cell surfaces, it migrated and self-assembled into exosome-like aggregates at certain locations on the cell membranes. Studies using confocal microscopy and scanning electron microscopy revealed that peptide PTP-7b induced cell tissue damage through a new cell lysis mechanism that involved peptide self-assembly on cell surfaces, extracting lipids from cell membranes, and transporting peptides into the cytoplasm. Peptide self-assembly attributed greatly to peptide-cell interactions and thus the biological activity of a peptide. Because peptide self-assembly was a slow process, PTP-7b-induced cell lysis showed a biphasic behavior: a gradual viability decrease was followed by a rapid decline. These results suggest that peptide self-assembly could be equally as important as charge and secondary structure of a peptide in determining the anticancer and antibacterial activities of therapeutic peptides.

- 3D Direct Laser Writing of Nano- and Microstructured Hierarchical Gecko-Mimicking Surfaces

Röhrig, M.; Thiel, M.; Worgull, M.; Hölscher, H. *Small* **2012**, *8*, 3009–3015.

Abstract:

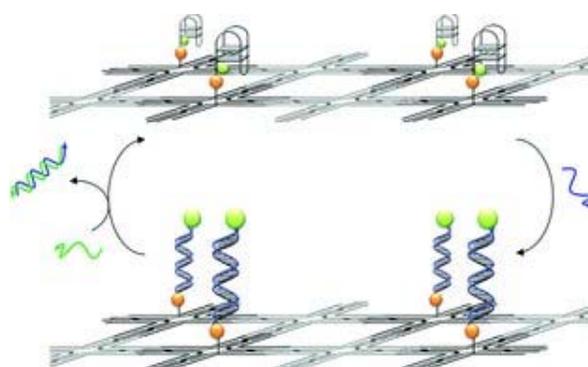


Applying 3D direct laser writing, artificial hierarchical gecko-type structures are designed and fabricated down to nanometer dimensions. In this way, the elastic modulus and the length scale of the gecko's setae are very closely matched. Direct laser writing is a very flexible rapid prototyping method allowing the fabrication of arbitrary nanostructures. Since the parameters of the structures can be easily changed, this technique is perfect for design studies of dry adhesives. Measuring the adhesional forces by atomic force microscopy, the influence of several design parameters like density, aspect ratio, and tip-shape on dry adhesion performance are systematically examined. In this way, it is revealed that hierarchy is favorable for artificial gecko-inspired dry adhesives made of stiff materials on the nanometer scale.

- Nanolattices of Switchable DNA-Based Motors

Saccà, B.; Siebers, B.; Meyer, R.; Bayer, M.; Niemeyer, C. M. *Small* **2012**, *8*, 3000–3008.

Abstract:

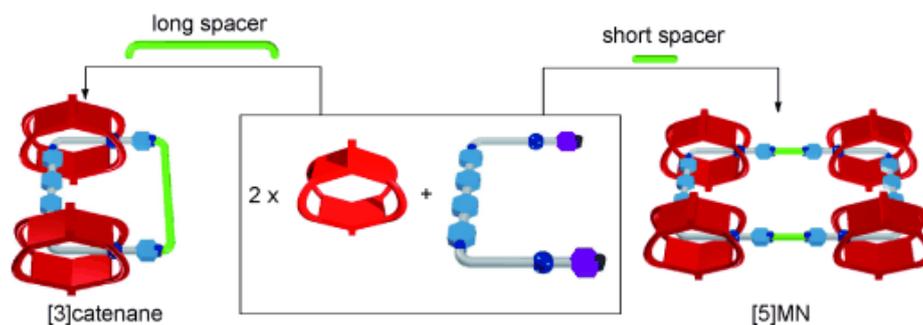


Miniaturization is an important aspect of device fabrication. Despite the advancements of modern top-down approaches, scaling-down to the sub-nanometer size is still a challenge. As an alternative, bottom-up approaches, such as the use of DNA as an engineering material, are therefore emerging, allowing control of matter at the single-molecule level. A DNA-based self-assembly method for the construction of switchable DNA devices is described here based on G-quadruplex moieties, which are patterned on quasi-planar DNA arrays with nanoscale precision. The reversible switching of the devices is triggered by addition of DNA sequences ('fuels') and translated into linear extension/contractile movements. The conformational change of the devices was visualized by atomic force microscopy and FRET spectroscopy. Steady state fluorescence spectroscopy indicated that scaffolding of the G4 motors to either individual tiles or extended superlattices had no significant impact on the switching and optical performance of the system. However, time-resolved spectroscopy revealed that ordering in the microstructural environment enhances the fraction of molecules subject to FRET. Altogether, our study confirms that DNA superstructures are well-suited scaffolds for accommodation of mechanically switchable units and thus opens the door to the development of more sophisticated nanomechanical devices.

- Using Host–Guest Complexation to Fold a Flexible Linear Organic String: Kinetically Controlled Syntheses of [3]Catenanes and a Five-Membered Molecular Necklace

Chang, C.-F.; Chuang, C.-J.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Angew. Chem. Int. Ed.* **2012**, *51*, 10094-10098.

Abstract:

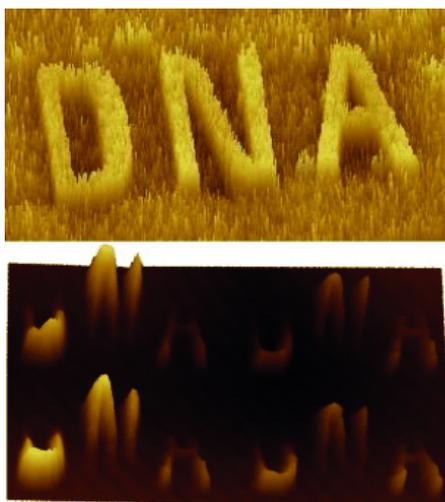


**Rings and necklaces:** Three [3]catenanes and a five-membered molecular necklace ([5]MN), with up to 60- and 92-membered rings as their centerpieces, respectively, have been synthesized. The synthesis started from the corresponding complexes in which the threaded flexible linear guests were bent at approximately right angles to facilitate kinetically controlled macrocyclizations.

- Fabrication of ssDNA/Oligo(ethylene glycol) Monolayers and Complex Nanostructures by an Irradiation-Promoted Exchange Reaction

Khan, M. N.; Tjong, V.; Chilkoti, A.; Zharnikov, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 10303-10306.

Abstract:

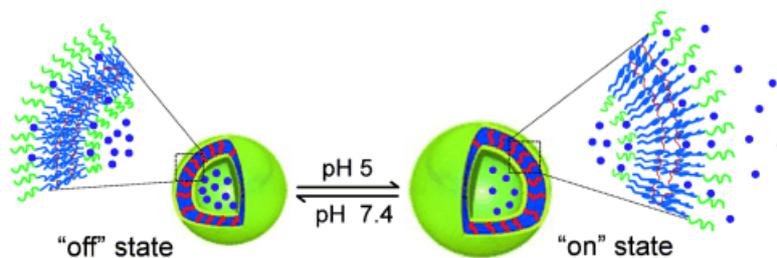


**Creative design:** An approach to preparing mixed monolayers of thiolated single-stranded DNA (ssDNA) and oligo(ethylene glycol)s (OEG-AT) in a broad range of compositions as well as ssDNA/OEG-AT patterns of any required shape (see top figure) has been shown. A combination of this approach with surface-initiated enzymatic polymerization allows complex 3D DNA nanostructures to be sculpted with high spatial precision (bottom).

- pH-Dependent Release of Doxorubicin from Fast Photo-Cross-Linkable Polymersomes Based on Benzophenone Units

Yassin, M. A.; Appelhans, D.; Mendes, R. G.; Rümmele, M. H.; Voit, B. *Chem. Eur. J.* **2012**, *18*, 12227–12231.

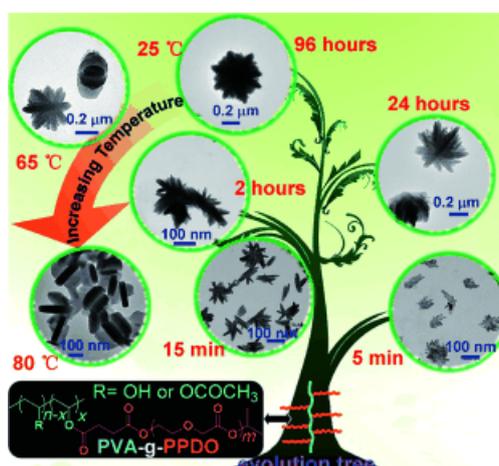
Abstract:



Conditional release: pH-Sensitive polymersomes are stabilized by cross-linking through short UV irradiation for reversible swelling/shrinking upon switching the pH. The membrane of these polymersomes behaves as a gate, which traffics the release of small bioactive molecules, such as doxorubicin from the lumen of polymersomes depending on cross-linking density and external pH (see scheme).

- Dynamic Origin and Thermally Induced Evolution of New Self-Assembled Aggregates from an Amphiphilic Comb-Like Graft Copolymer: A Multiscale and Multimorphological Procedure  
Wu, G.; Chen, S.-C.; Wang, X.-L.; Yang, K.-K.; Wang, Y.-Z. *Chem. Eur. J.* **2012**, *18*, 12237–12241.

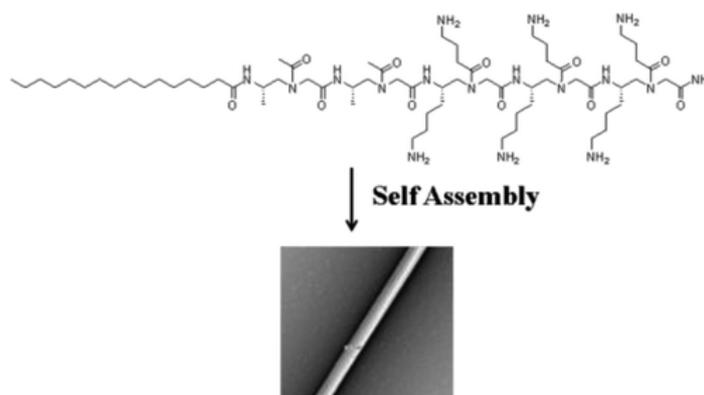
Abstract:



Snowflake's origin and evolution: New aggregates with a snowflake-like superstructure are prepared by facile and low-cost water-phase self-assembly of an amphiphilic comb-like graft copolymer, and their origin involving dynamic disorder–order structural evolution from nano- to microscale is revealed (see figure). Furthermore, aggregates perform a unique thermally induced multimorphological change leading to cluster-like nanostructures.

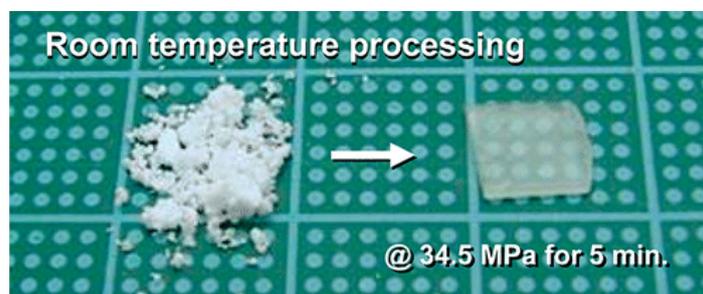
- Nanorods Formed from a New Class of Peptidomimetics  
Niu, Y.; Wu, H.; Huang, R.; Qiao, Q.; Costanza, P.; Wang, X.-S.; Hu, Y.; Amin, M. N.; Nguyen, A.-M.; Zhang, J.; Haller, E.; Ma, S.; Li, X.; Cai, J. *Macromolecules* **2012**, *45*, 7350–7355.

Abstract:



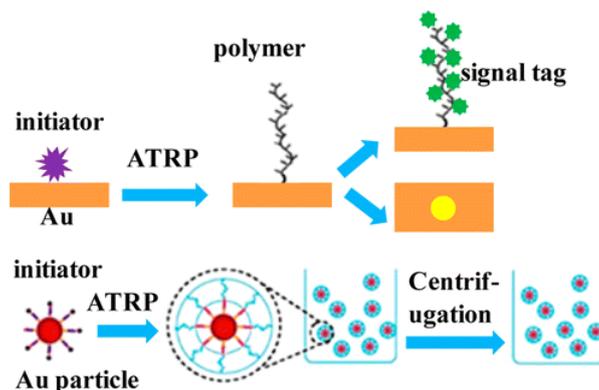
Although peptide amphiphiles have been explored as nanomaterials for different applications, nanostructures formed by hierarchical molecular assembly of sequence-specific peptidomimetics are much less developed. Such protein-like nanomaterials could enhance the current application of peptide-based amphiphiles by enriching the diversity of nanostructures, increasing *in vivo* stability for biomedical applications, and facilitating the understanding of biomacromolecular self-assembly. Herein we present a biomimetic  $\gamma$ -AApeptide amphiphile which forms nanorods. Our results demonstrate the capability of  $\gamma$ -AApeptide amphiphiles as a potential scaffold for the preparation of biomimetic and bioinspired nanostructures. The programmability and biocompatibility of  $\gamma$ -AApeptides could lead to novel nanomaterials for a wide variety of applications.

- Low-Temperature Processable Degradable Polyesters  
Taniguchi, I.; Lovell, N. G. *Macromolecules* **2012**, *45*, 7420–7428.  
Abstract:



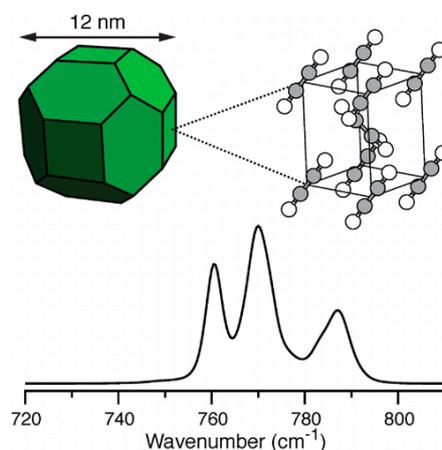
Block copolymers composed of a low- $T_g$  and high- $T_g$  block, with suitable pressure miscibility characteristics, can be formed at low temperature through the application of pressure. Aliphatic block copolyesters composed of poly( $\epsilon$ -caprolactone) derivatives and poly(L-lactide) show room temperature processability under hydraulic pressure of 34.5 MPa without polymer degradation. The mechanism of the pressure-induced flow is investigated by small-angle X-ray scattering. A scattering associated with a lamellae structure observed at ambient conditions decreases with elevating hydrostatic pressures, indicating pressure-induced phase mixing. Traces of the pressure-induced phase transition are studied by differential scanning calorimetry and X-ray diffraction. Tensile test of the block copolymers reveals that the mechanical properties can be readily controlled by changing composition, molecular weight, and chemical structure of the blocks. Among them, the hard segment PLLA fraction is the key factor to characterize the properties. Young's modulus of the block copolyesters is similar to that of polyethylene.

- Target-Triggered Polymerization for Biosensing  
Wu, Y.; Wei, W.; Liu, S. *Acc. Chem. Res.* **2012**, *45*, 1441-1450.

Abstract:

Because of the potential applications of biosensors in clinical diagnosis, biomedical research, environmental analysis, and food quality control, researchers are very interested in developing sensitive, selective, rapid, reliable, and low-cost versions of these devices. A classic biosensor directly transduces ligand–target binding events into a measurable physical readout. Because of the limited detection sensitivity and selectivity in earlier biosensors, researchers have developed a number of sensing/signal amplification strategies. Through the use of nanostructured or long chain polymeric materials to increase the upload of signal tags for amplification of the signal readout associated with the ligand–target binding events, researchers have achieved high sensitivity and exceptional selectivity. In this Account, we summarize a series of electrochemical and optical biosensors that employ target-triggered polymerization. We focus on the use of atom transfer radical polymerization (ATRP), as well as activator generated electron transfer for atom transfer radical polymerization (AGET ATRP) for in-situ formation of polymer materials for optically or electrochemically transducing DNA hybridization and protein–target binding. ATRP and AGET ATRP can tolerate a wide range of functional monomers. They also allow for the preparation of well-controlled polymers with narrow molecular weight distribution, which was predetermined by the concentration ratio of the consumed monomer to the introduced initiator. Because the reaction initiator can be attached to a variety of detection probes through well-established cross-linking reactions, this technique could be expanded as a universal strategy for the sensitive detection of DNA and proteins. We see enormous potential for this new sensing technology in the development of portable DNA/protein sensors for point-of-need applications

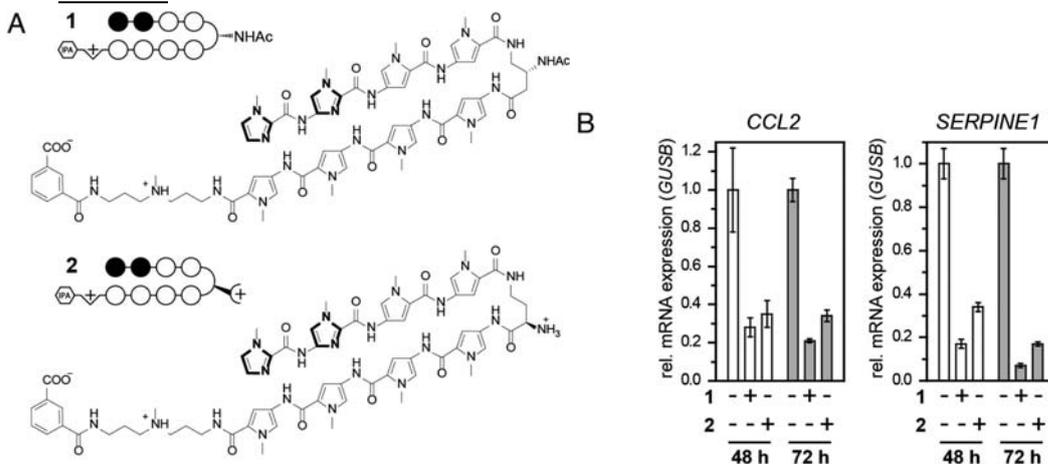
- From Plasmon Spectra of Metallic to Vibron Spectra of Dielectric Nanoparticles  
Preston, T. C.; Signorell, R. *Acc. Chem. Res.* **2012**, *45*, 1501-1510.

Abstract:

Light interacts surprisingly differently with small particles than with bulk or gas phase materials. This can cause rare phenomena such as the occurrence of a “blue moon”. Spectroscopic particle phenomena of similar physical origin have also spawned countless applications ranging from remote sensing to medicine. Despite the broad interest in particle spectra, their interpretation still poses many challenges. In this Account, we discuss the challenges associated with the analysis of infrared, or vibron, extinction spectra of small dielectric particles.

- Gene expression changes in a tumor xenograft by a pyrrole-imidazole polyamide  
Raskatov, J. A.; Nickols, N. G.; Hargrove, A. E.; Marinov, G. K.; Wold, B.; Dervan, P. B. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 16041-16045.

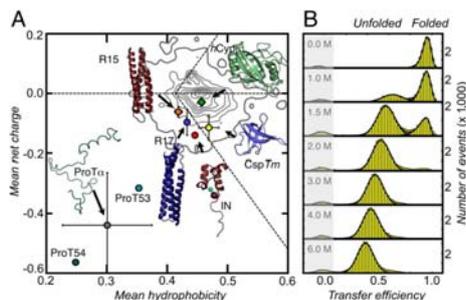
Abstract:



Gene regulation by DNA binding small molecules could have important therapeutic applications. This study reports the investigation of a DNA-binding pyrrole-imidazole polyamide targeted to bind the DNA sequence 5'-WGGWWW-3' with reference to its potency in a subcutaneous xenograft tumor model. The molecule is capable of trafficking to the tumor site following subcutaneous injection and modulates transcription of select genes in vivo. An FITC-labeled analogue of this polyamide can be detected in tumor-derived cells by confocal microscopy. RNA deep sequencing (RNA-seq) of tumor tissue allowed the identification of further affected genes, a representative panel of which was interrogated by quantitative reverse transcription-PCR and correlated with cell culture expression levels.

- Polymer scaling laws of unfolded and intrinsically disordered proteins quantified with single-molecule spectroscopy  
Hofmann, H.; Soranno, A.; Borgia, A.; Gast, K.; Nettels, D.; Schuler, B. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 16155-16160.

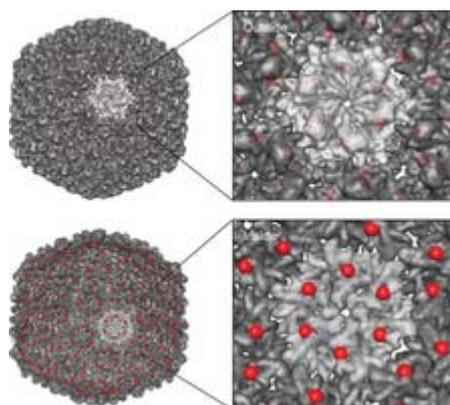
Abstract:



The dimensions of unfolded and intrinsically disordered proteins are highly dependent on their amino acid composition and solution conditions, especially salt and denaturant concentration. However, the quantitative implications of this behavior have remained unclear, largely because the effective theta-state, the central reference point for the underlying polymer collapse transition, has eluded experimental determination. Here, we used single-molecule fluorescence spectroscopy and two-focus correlation spectroscopy to determine the theta points for six different proteins. While the scaling exponents of all proteins converge to  $0.62 \pm 0.03$  at high denaturant concentrations, as expected for a polymer in good solvent, the scaling regime in water strongly depends on sequence composition. The resulting average scaling exponent of  $0.46 \pm 0.05$  for the four foldable protein sequences in our study suggests that the aqueous cellular milieu is close to effective theta conditions for unfolded proteins. In contrast, two intrinsically disordered proteins do not reach the  $\Theta$ -point under any of our solvent conditions, which may reflect the optimization of their expanded state for the interactions with cellular partners. Sequence analyses based on our results imply that foldable sequences with more compact unfolded states are a more recent result of protein evolution.

- Use of the interior cavity of the P22 capsid for site-specific initiation of atom-transfer radical polymerization with high-density cargo loading  
Lucon, J.; Qazi, S.; Uchida, M.; Bedwell, G. J.; LaFrance, B.; Prevelige Jr, P. E.; Douglas, T. *Nature Chem.* **2012**, *4*, 781–788.

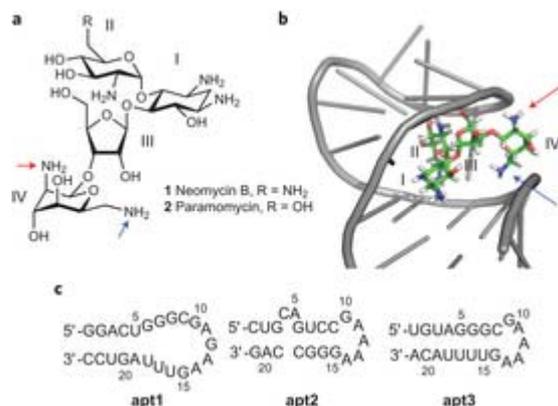
Abstract:



Virus-like particles (VLPs) have emerged as important and versatile architectures for chemical manipulation in the development of functional hybrid nanostructures. Here we demonstrate a successful site-selective initiation of atom-transfer radical polymerization reactions to form an addressable polymer constrained within the interior cavity of a VLP. Potentially, this protein–polymer hybrid of P22 and cross-linked poly(2-aminoethyl methacrylate) could be useful as a new high-density delivery vehicle for the encapsulation and delivery of small-molecule cargos. In particular, the encapsulated polymer can act as a scaffold for the attachment of small functional molecules, such as fluorescein dye or the magnetic resonance imaging (MRI) contrast agent Gd-diethylenetriaminepentacetate, through reactions with its pendant primary amine groups. Using this approach, a significant increase in the labelling density of the VLP, compared to that of previous modifications of VLPs, can be achieved. These results highlight the use of multimeric protein–polymer conjugates for their potential utility in the development of VLP-based MRI contrast agents with the possibility of loading other cargos.

- Selective transformations of complex molecules are enabled by aptameric protective groups  
Bastian, A. A.; Marcozzi, A.; Herrmann, A. *Nature Chem.* **2012**, *4*, 789–793.

Abstract:



Emerging trends in drug discovery are prompting a renewed interest in natural products as a source of chemical diversity and lead structures. However, owing to the structural complexity of many natural compounds, the synthesis of derivatives is not easily realized. Here, we demonstrate a conceptually new approach using oligonucleotides as aptameric protective groups. These block several functionalities by non-covalent interactions in a complex molecule and enable the highly chemo- and regioselective derivatization (>99%) of natural antibiotics in a single synthetic step with excellent conversions of up to 83%. This technique reveals an important structure–activity relationship in neamine-based antibiotics and should help both to accelerate the discovery of new biologically active structures and to avoid potentially costly and cumbersome synthetic routes.

- One-Pot Synthesis of Amides from Aldehydes and Amines via C–H Bond Activation  
Cadoni, R.; Porcheddu, A.; Giacomelli, G.; De Luca, L. *Org. Lett.* **2012**, *14*, 5014–5017.

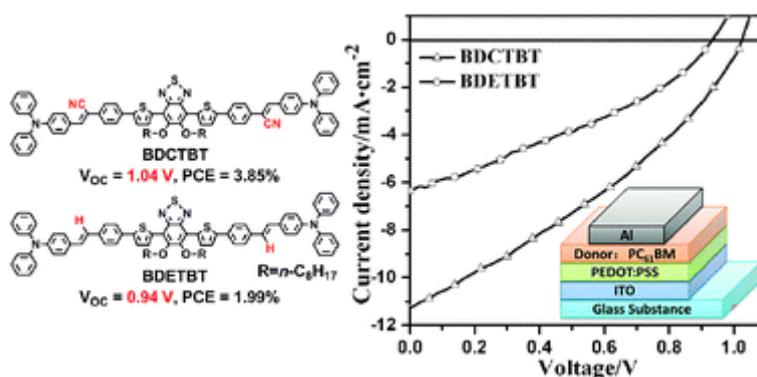
Abstract:



A one-pot synthesis of amides from aldehydes with N-chloroamines, prepared in situ from amines, has been developed. Both aliphatic and aromatic aldehydes and many types of mono- and disubstituted amines are tolerant in this transformation. This cross-coupling reaction appears simple and convenient, has a wide substrate scope and makes use of cheap, abundant, and easily available reagents.

- D–π–A–π–D type benzothiadiazole–triphenylamine based small molecules containing cyano on the π-bridge for solution-processed organic solar cells with high open-circuit voltage  
Zeng, S.; Yin, L.; Ji, C.; Jiang, X.; Li, K.; Li, Y.; Wang, Y. *Chem. Commun.* **2012**, *48*, 10627–10629.

Abstract :

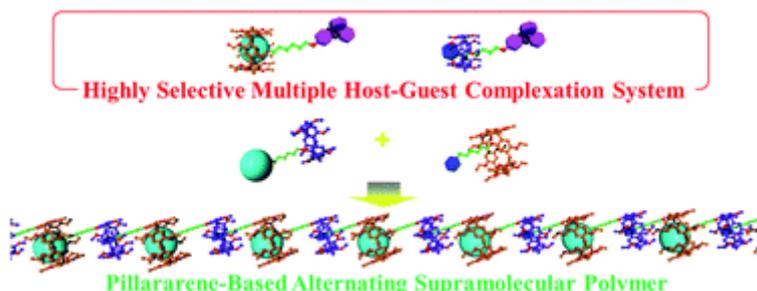


Two novel D- $\pi$ -A- $\pi$ -D structured small molecules composed of benzothiadiazole and triphenylamine were designed and synthesized. BDCTBT with cyano on the  $\pi$ -bridge exhibited a deep HOMO energy level, resulting in an impressive  $V_{OC}$  of up to 1.04 V with a PCE of 3.85%, while non-cyano substituted BDETBT yielded a  $V_{OC}$  of 0.94 V and a PCE of 1.99%.

- Supramolecular polymers with alternating pillar[5]arene and pillar[6]arene units from a highly selective multiple host-guest complexation system and monofunctionalized pillar[6]arene

Ogoshi, T.; Kayama, H.; Yamafuji, D.; Aoki, T.; Yamagishi, T. *Chem. Sci.* **2012**, *3*, 3221–3226.

Abstract :



A highly selective multiple host-guest complexation system based on pillar[5]arene and pillar[6]arene is reported. A pyridinium cation moiety is included in the pillar[5]arene cavity, but hardly forms a stable host-guest complex with pillar[6]arene. A 1,4-diazabicyclo[2.2.2]octane cation moiety forms a host-guest complex with pillar[6]arene, but not with pillar[5]arene. A synthetic route to mono-reactive pillar[6]arene is also developed, enabling the synthesis of pillar[6]arene with a pyridinium cation group at a single position. Based on the highly selective multiple host-guest complexation system and mono-reactive pillar[6]arene, a supramolecular polymer with alternating pillar[5]arene and pillar[6]arene units is constructed.

- Dialkyl-14H-benzo[4,5]isoquino[2,3-a]perimidin-14-one-3,4,10,11-tetracarboxylic diimides: A New Family of n-Type Organic Semiconductors

Zhu, M.; Zhang, J.; Yu, G.; Chen, H.; Huang, J.; Liu., Y. *Chem. Asian J.* **2012**, *7*, 2208-2212.

Abstract:

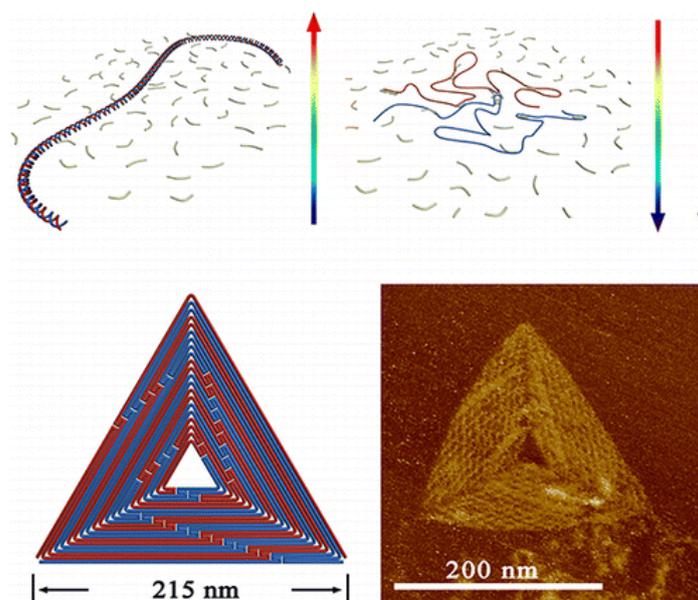


Starting a family: A novel family of asymmetric arylenediimides, dialkyl-14H-benzo[4,5]isoquino[2,3-a]perimidin-14-one-3,4,10,11-tetracarboxylic diimides (BIPO-DI), was successfully designed and synthesized. The effects of different alkyl substitution on the structures were characterized by UV/Vis absorption spectroscopy and cyclic voltammetry. Field-effect transistors based on di-n-octyl BIPO-DI thin films show an electron mobility of  $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with a high current on/off ratio of 108.

- DNA Origami with Double-Stranded DNA As a Unified Scaffold

Yang, Y.; Han, D.; Nangreave, J.; Liu, Y.; Yan, H. *ACS Nano* **2012**, *6*, 8209-8215.

Abstract:

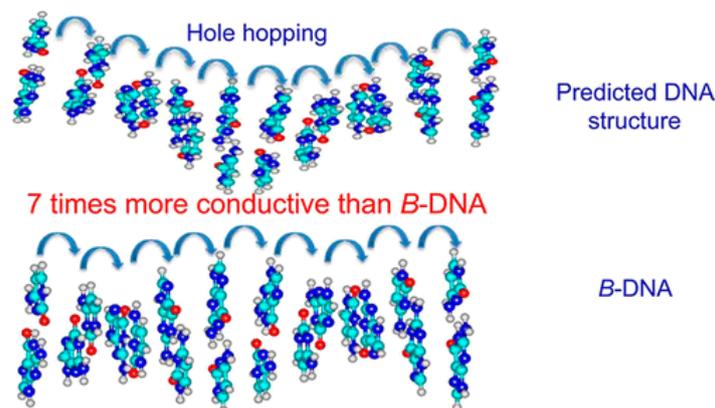


Scaffolded DNA origami is a widely used technology for self-assembling precisely structured nanoscale objects that contain a large number of addressable features. Typical scaffolds are long, single strands of DNA (ssDNA) that are folded into distinct shapes through the action of many, short ssDNA staples that are complementary to several different domains of the scaffold. However, sources of long single-stranded DNA are scarce, limiting the size and complexity of structures that can be assembled. Here we demonstrated that dsDNA (double-stranded DNA) scaffolds can be directly used to fabricate integrated DNA origami structures that incorporate both of the constituent ssDNA molecules. Two basic principles were employed in the design of scaffold folding paths: folding path asymmetry and periodic convergence of the two ssDNA scaffold strands. Asymmetry in the folding path minimizes unwanted complementarity between staples, and incorporating an offset between the folding paths of each ssDNA scaffold strand reduces the number of times that complementary portions of the strands are brought into close proximity with one another, both of

which decrease the likelihood of dsDNA scaffold recovery. Meanwhile, the folding paths of the two ssDNA scaffold strands were designed to periodically converge to promote the assembly of a single, unified structure rather than two individual ones. Our results reveal that this basic strategy can be used to reliably assemble integrated DNA nanostructures from dsDNA scaffolds.

- DNA Base Pair Stacks with High Electric Conductance: A Systematic Structural Search  
Berlin, Y. A.; Voityuk, A. A.; Ratner, M. A. *ACS Nano* **2012**, *6*, 8216-8225.

Abstract:

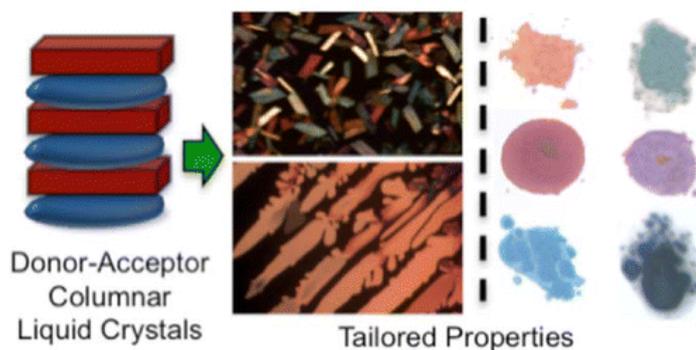


We report a computational search for DNA  $\pi$ -stack structures exhibiting high electric conductance in the hopping regime, based on the INDO/S calculations of electronic coupling and the method of data analysis called k-means clustering. Using homogeneous poly(G)–poly(C) and poly(A)–poly(T) stacks as the simplest structural models, we identify the configurations of neighboring G:C and A:T pairs that allow strong electronic coupling and, therefore, molecular electric conductance much larger than the values reported for the corresponding reference systems in the literature. A computational approach for modeling the impact of thermal fluctuations on the averaged dimer structure was also proposed and applied to the [(G:C),(G:C)] and [(A:T),(A:T)] duplexes. The results of this work may provide guidance for the construction of DNA devices and DNA-based elements of nanoscale molecular circuits. Several factors that cause changes of step parameters favorable to the formation of the predicted stack conformation with high electric conductance of DNA molecules are also discussed; favorable geometries may enhance the conductivity by factors as large as 15.

- Predictable Tuning of Absorption Properties in Modular Aromatic Donor–Acceptor Liquid Crystals

Leigh, K. R.; Esarey, B. E.; Murray, A. E.; Reczek, J. J. *Chem. Mater.* **2012**, *24*, 3318–3328.

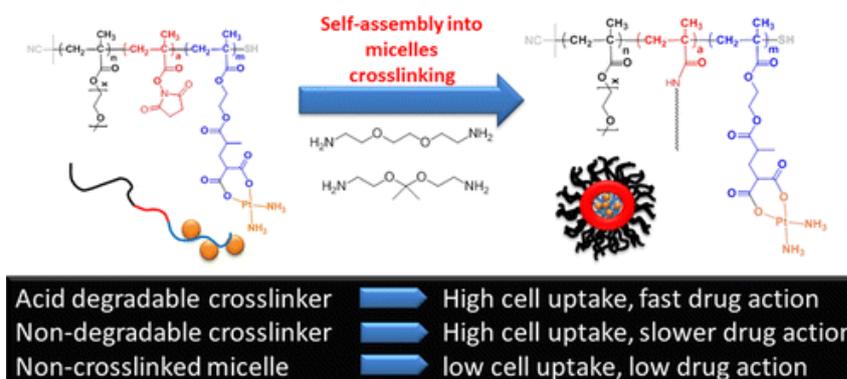
Abstract:



This paper demonstrates a combinatorial design strategy in the generation of columnar liquid crystalline materials with tailored properties based on the molar (1:1) combination of complementary electron-rich and electron-poor aromatic components. Through the iterative study of relationships of individual component structure to combined material properties, a series of aromatic donor–acceptor columnar liquid crystal materials was developed whose charge-transfer absorption completely spans the visible spectrum. The red-onset of absorption in these materials is shown to correlate closely with straightforward orbital energy level calculations (density functional theory) of individual component molecules. This holds equally true regardless of the component or range of absorption characteristics exhibited by the molecules of this study. Charge-transfer band extinction coefficients are substantial in these materials, ranging from 3800–15500 M<sup>-1</sup>; the magnitude of which is shown to correlate to component identity. This ability to predictably design a range of functional material properties through preceding calculations, and achieving a tailored diversity of properties through combination of relatively simple component molecules, provides an impressive array of new materials and exemplifies this as a powerful strategy for efficient, targeted material design.

- Acid Degradable Cross-Linked Micelles for the Delivery of Cisplatin: A Comparison with Nondegradable Cross-Linker  
Huynh, V. T.; Binauld, S.; de Souza, P. L.; Stenzel, M. H. *Chem. Mater.* **2012**, *24*, 3197–3211.

Abstract:



Well-defined and nontoxic cross-linked polymeric micelles, containing either permanent or acid degradable cross-linkers, were employed for efficient intracellular delivery of cisplatin. The self-assembled structures were generated from triblock copolymers of poly(oligo(ethylene glycol) methylether methacrylate)-block-poly(N-hydroxysuccinic methacrylate)-block-poly(1,1-di-tert-butyl 3-(2-(methacryloyloxy)ethyl) butane-1,1,3-tricarboxylate) (POEGMEMA-b-PNHSMA-b-PMAETC) loaded with cisplatin. The polymeric micelles were subsequently cross-linked via a reaction between pendant activated esters at the nexus core of the triblock copolymer using acid degradable ketal diamino cross-linkers. An in vitro study confirmed that both uncross-linked and cross-linked micelles prior to the loading of the platinum drug were nontoxic against OVCAR-3 cells even at high polymer concentration (around 300  $\mu\text{g mL}^{-1}$ ). The drug loaded cross-linked platinum polymeric micelles were superior to the uncross-linked platinum polymeric micelles in terms of cytotoxicity against OVCAR-3, due to a higher cellular uptake. Although there was no significant difference in cytotoxicity of cross-linked platinum polymeric micelles using different cross-linkers (permanent and acid cleavable) after 72 h of exposure, the difference was noticeable after 24 h of incubation, highlighting a much higher activity for acid degradable cross-linked micelles with conjugated platinum drugs. Moreover, the clonogenic assay suggested that cross-linked micelle loaded platinum

drugs, in contrast to uncross-linked micelles, can effectively inhibit the OVCAR-3 cell regrowth for an extended period of time (10 days), even at very low micellar concentrations. In summary, acid degradable linkers ensure high cellular uptake compared to uncross-linked micelles but also lead to a faster drug action in comparison to a permanently cross-linked micelle.