

- *Shewanella oneidensis* MR-1 bacterial nanowires exhibit p-type, tunable electric behavior
Leung, K. M.; Wagner, G.; El-Nagger, M. Y.; Gorby, Y.; Southam, G.; Lau, W. M.; Yang, J. *Nano Lett.* **2013**, *13*, 2407-2411.

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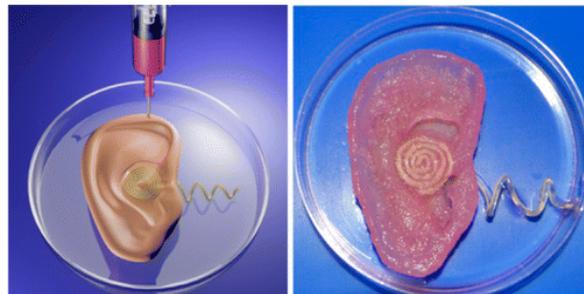
Abstract:



The study of electrical transport in biomolecular materials is critical to our fundamental understanding of physiology and to the development of practical bioelectronics applications. In this study, we investigated the electronic transport characteristics of *Shewanella oneidensis* MR-1 nanowires by conducting-probe atomic force microscopy (CP-AFM) and by constructing field-effect transistors (FETs) based on individual *S. oneidensis* nanowires. Here we show that *S. oneidensis* nanowires exhibit p-type, tunable electronic behavior with a field-effect mobility on the order of $10^{-1} \text{ cm}^2/(\text{V s})$, comparable to devices based on synthetic organic semiconductors. This study opens up opportunities to use such bacterial nanowires as a new semiconducting biomaterial for making bioelectronics and to enhance the power output of microbial fuel cells through engineering the interfaces between metallic electrodes and bacterial nanowires.

- 3D printed bionic ears
Mannoor, M. S.; jiang, Z.; James, T.; kong, Y. L.; Malatesta, K. A.; Soboyejo, W. O.; Verma, N.; Gracias, D. H.; McAlpine, M. C. *Nano Lett.* **2013**, *13*, 2634-2639.

Abstract:



The ability to three-dimensionally interweave biological tissue with functional electronics could enable the creation of bionic organs possessing enhanced functionalities over their human counterparts. Conventional electronic devices are inherently two-dimensional, preventing seamless multidimensional integration with synthetic biology, as the processes and materials are very different. Here, we present a novel strategy for overcoming these difficulties via additive manufacturing of biological cells with structural and nanoparticle derived electronic elements. As a proof of concept, we generated a bionic ear via 3D printing of a cell-seeded hydrogel matrix in the anatomic geometry of a human ear, along with an intertwined conducting polymer consisting of infused silver nanoparticles. This allowed for in vitro culturing of cartilage tissue around an inductive coil antenna in the ear, which subsequently enables readout of inductively-coupled signals from cochlea-shaped electrodes. The printed ear exhibits enhanced auditory sensing for radio frequency reception, and complementary left and right ears can listen to stereo audio music. Overall, our

approach suggests a means to intricately merge biologic and nanoelectronic functionalities via 3D printing.

- Sustainable Polymers: Opportunities for the Next Decade
Miller, S. A. *ACS Macro Lett.* **2013**, *2*, 550-554.

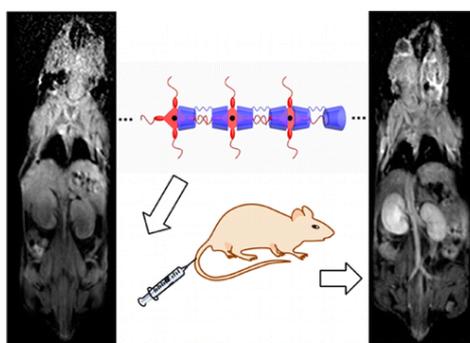
Abstract:



The field of sustainable polymers is growing and evolving at unprecedented rates. Researchers are increasingly concerned with the feedstock origins and the degradation behavior of, especially, large-scale commodity packaging plastics. A perspective is offered here for the design of sustainable polymers, specifically addressing opportunities for monomer development and polymer degradation. Key concepts include: water degradability instead of biodegradability; incorporation of novel main-chain functionality, such as acetals; utilization of lignin-based aromatics; and direct polymerization of biogenic C1 feedstocks.

- Construction of a Supramolecular Polymer by Bridged Bis(permethyl- β -cyclodextrin)s with Porphyrins and Its Highly Efficient Magnetic Resonance Imaging.
Sun, M.; Zhang, H.-Y.; Liu, B.-W.; Liu, Y. *Macromolecules* **2013**, *46*, 4268-4275.

Abstract:



Supramolecular polymer as an MRI contrast agent

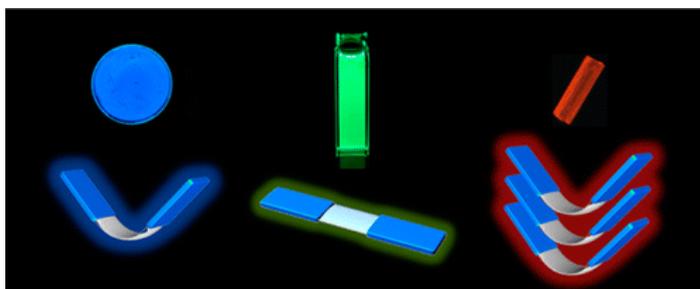
A supramolecular polymer is first constructed through the intermolecular inclusion complexation of bridged bis(permethyl- β -cyclodextrin) (**1**) with Mn^{III} -porphyrin bearing poly(ethylene glycol) (PEG) side chains (Mn^{III} -TPP) and characterized by UV/vis absorption spectroscopy, NMR, dynamic light scattering (DLS), atomic force microscopy (AFM), and transmission electron microscopy (TEM). Mn^{III} -TPP in the supramolecular polymer **1**· Mn^{III} -TPP would be reduced effectively to a higher electronic spins Mn^{II} -TPP by sodium ascorbate, but free Mn^{III} -TPP cannot be reduced in the same condition. The toxicity of the supramolecular polymer *in vitro* and the magnetic resonance imaging effectiveness both *in vitro* and *in vivo* are estimated, and the results obtained not only demonstrate the supramolecular polymer to have no cellular toxicity but also show the MR signal enhancement.

- A π -Conjugated System with Flexibility and Rigidity That Shows Environment-Dependent RGB

Luminescence

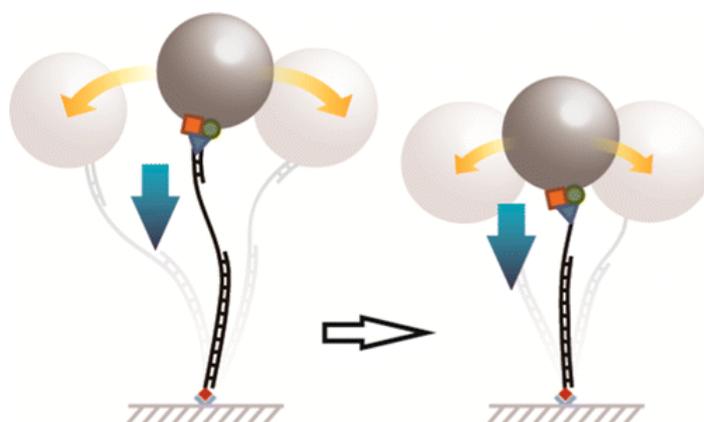
Yuan, C.; Saito, S.; Camacho, C.; Irle, S.; Hisaki, I.; Yamaguchi, S. *J. Am. Chem. Soc.* **2013**, *135*, 8842–8845.

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Abstract:

We have designed and synthesized a π -conjugated system that consists of a flexible and nonplanar π joint and two emissive rigid and planar wings. This molecular system exhibits respectively red, green, and blue (RGB) emission from a single-component luminophore in different environments, namely in polymer matrix, in solution, and in crystals. The flexible unit gives rise to a dynamic conformational change in the excited state from a nonplanar V-shaped structure to a planar structure, leading to a dual fluorescence of blue and green colors. The rigid and planar moieties favor the formation of a two-fold π -stacked array of the V-shaped molecules in the crystalline state, which produces a red excimer-like emission. These RGB emissions are attained without changing the excitation energy.

- Direct Observation of RecBCD Helicase as Single-Stranded DNA Translocases
Chung, C.; Li, H.-W. *J. Am. Chem. Soc.* **2013**, *135*, 8920–8925.

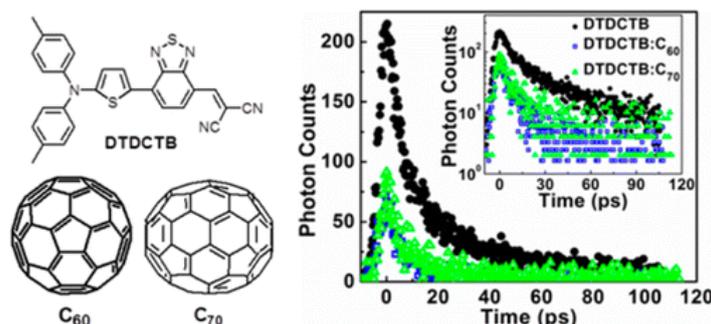
Abstract:

The heterotrimeric *Escherichia coli* RecBCD enzyme comprises two helicase motors with different polarities: RecB (3'-to-5') and RecD (5'-to-3'). This superfamily I helicase is responsible for initiating DNA double-strand-break (DSB) repair in the homologous recombination pathway. We used single-molecule tethered particle motion (TPM) experiments to visualize the RecBCD helicase translocation over long single-stranded (ss) DNA (>200 nt) with no apparent secondary structure. The bead-labeled RecBCD helicases were found to bind to the surface-immobilized blunt-end DNA, and translocate along the DNA substrates containing an ssDNA gap, resulting in a gradual decrease in the bead Brownian motion. Successful observation of RecBCD translocation over a long gap in either 3'-to-5' or 5'-to-3' ssDNA direction indicates that RecBCD helicase possesses ssDNA translocase activities in both polarities. Most RecBCD active tethers showed full translocation across the ssDNA to the dsDNA region, with about 19% of enzymes dissociated from the ss/dsDNA junction after translocating across the ssDNA region. In addition, we prepared DNA substrates containing two opposite polarities (5'-to-

3' and 3'-to-5') of ssDNA regions intermitted by duplex DNA. RecBCD was able to translocate across both ssDNA regions in either ssDNA orientation orders, with less than 40% of tethers dissociating when entering into the second ssDNA region. These results suggest a model that RecBCD is able to switch between ssDNA translocases and rethread the other strand of ssDNA.

- Charge Carrier Dynamics of Vapor-Deposited Small-Molecule/Fullerene Organic Solar Cells
Chang, A. Y.; Chen, Y.-H.; Lin, H.-W.; Lin, L.-Y.; Wong, K.-T.; Schaller, R. D. *J. Am. Chem. Soc.* **2013**, *135*, 8790–8793.

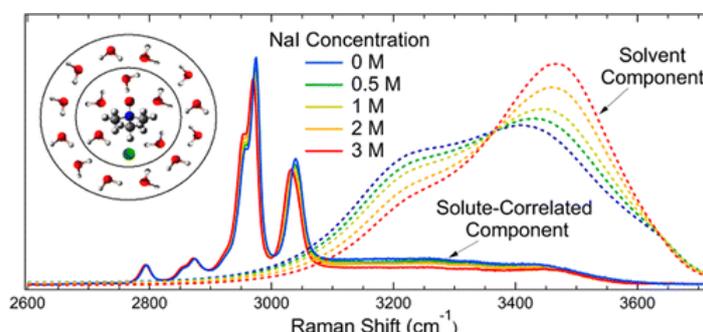
Abstract:



Although small-molecule organic solar cells (SMOSCs) have shown increasingly promising prospects as a source of solar power, there have been few studies concerning the photophysics of these systems. Here, we report the time scale and efficiency of charge separation and recombination in a vapor-deposited SMOSC material that produces 5.81% power conversion efficiency. Transient absorption and time-resolved photoluminescence (trPL) studies of thin film blends comprising DTDCTB, a narrow-band gap electron donor, and either C₆₀ or C₇₀ as an electron acceptor show that charge separation occurs in ~ 100 fs, while charge recombination takes place over sub-ns and ns time scales. trPL indicates a donor electron–hole pair lifetime of ~ 33 ps in the neat film and reveals that $\sim 20\%$ of donors fail to charge separate in donor–acceptor mixed films, likely owing to some spatially extended donor-rich regions that interact poorly with acceptors. Our results suggest that morphological manipulations of this material could further improve device efficiency.

- Expulsion of Ions from Hydrophobic Hydration Shells
Rankin, B. M.; Ben-Amotz, D. *J. Am. Chem. Soc.* **2013**, *135*, 8818–8821.

Abstract:

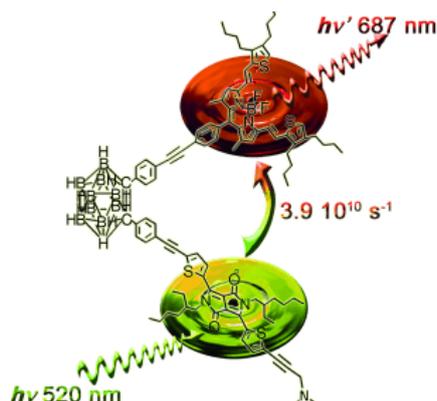


Raman spectroscopy is combined with multivariate curve resolution to quantify interactions between ions and molecular hydrophobic groups in water. The molecular solutes in this study all have similar structures, with a trimethyl hydrophobic domain and a polar or charged headgroup. Our results imply that aqueous sodium and fluoride ions are strongly expelled from the first hydration shells of the hydrophobic (methyl) groups, while iodide ions are found to enter the hydrophobic hydration shell,

to an extent that depends on the methyl group partial charge. However, our quantitative estimates of the corresponding ion binding equilibrium constants indicate that the iodide concentration in the first hydrophobic hydration shell is generally lower than that in the surrounding bulk water, and so an iodide ion cannot be viewed as having a true affinity for the molecular hydrophobic interface, but rather is less strongly expelled from such an interface than fluoride.

- Through-Space Electronic Energy Transfer Across Proximal Molecular Dyads
Harriman, A.; Alamiry, M. A. H.; Hagon, J. P.; Hablot, D.; Ziessel, R. *Angew. Chem. Int. Ed.* **2013**, 52, 6611–6615.

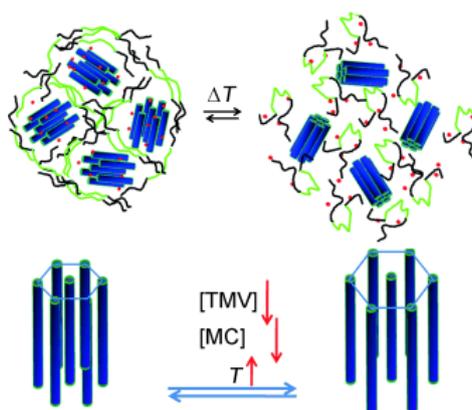
Abstract:



Energy transfer: For large electronic systems in close proximity it is shown that the coulombic mechanism accounts for the rates of electronic energy transfer for both linear and perpendicular geometries across distances from 36 to 16 Å. Replacing the ideal dipole approximation with either a revised extended dipole or atom-localized charges improves agreement between theory and experiment.

- Biomolecular Assembly of Thermoresponsive Superlattices of the Tobacco Mosaic Virus with Large Tunable Interparticle Distances
Li, T.; Zan, X.; Winans, R. E.; Wang, Q.; Lee, B. *Angew. Chem. Int. Ed.* **2013**, 52, 6638–6642.

Abstract:

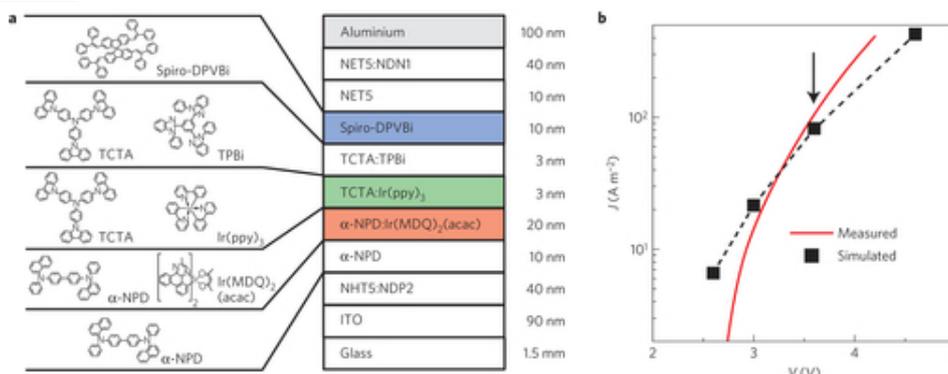


Not too friendly with their neighbors: In the presence of certain polymers, such as methyl cellulose (MC), the rodlike tobacco mosaic virus (TMV) formed a superlattice in which the distance between the virus particles could be controlled within a wide range up to approximately 5 times their diameter. The spacing between the TMV particles in the superlattice showed a unique dependence on temperature and on the concentration of TMV (see picture).

- Molecular-scale simulation of electroluminescence in a multilayer white organic light-emitting diode

Mesta, M.; Carvelli, M.; de Vries, R. J.; van Eersel, H.; van der Holst, J. J. M.; Schober, M.; Furno, M.; Lüsse, B.; Leo, K.; Loebel, P.; Coehoorn, R.; Bobbert, P. A. *Nature Mater.* **2013**, *12*, 652–658.

Abstract:

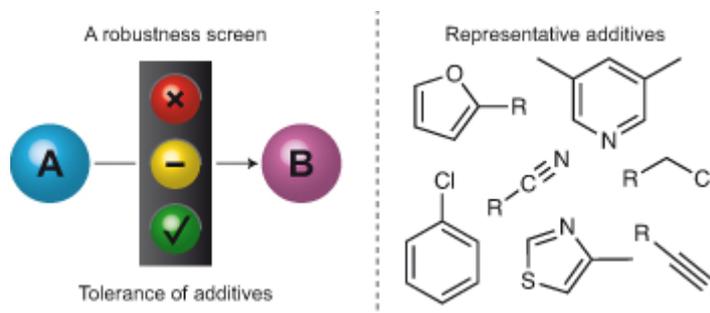


In multilayer white organic light-emitting diodes the electronic processes in the various layers— injection and motion of charges as well as generation, diffusion and radiative decay of excitons— should be concerted such that efficient, stable and colour-balanced electroluminescence can occur. Here we show that it is feasible to carry out Monte Carlo simulations including all of these molecular-scale processes for a hybrid multilayer organic light-emitting diode combining red and green phosphorescent layers with a blue fluorescent layer. The simulated current density and emission profile are shown to agree well with experiment. The experimental emission profile was obtained with nanometre resolution from the measured angle- and polarization-dependent emission spectra. The simulations elucidate the crucial role of exciton transfer from green to red and the efficiency loss due to excitons generated in the interlayer between the green and blue layers. The perpendicular and lateral confinement of the exciton generation to regions of molecular-scale dimensions revealed by this study demonstrate the necessity of molecular-scale instead of conventional continuum

- A robustness screen for the rapid assessment of chemical reactions

Collins, K. D.; Glorius, F. *Nature Chem.* **2013**, *5*, 597–601.

Abstract:



In contrast to the rapidity with which scientific information is published, the application of new knowledge often remains slow, and we believe this to be particularly true of newly developed synthetic organic chemistry methodology. Consequently, methods to assess and identify robust chemical reactions are desirable, and would directly facilitate the application of newly reported synthetic methodology to complex synthetic problems. Here, we describe a simple process for

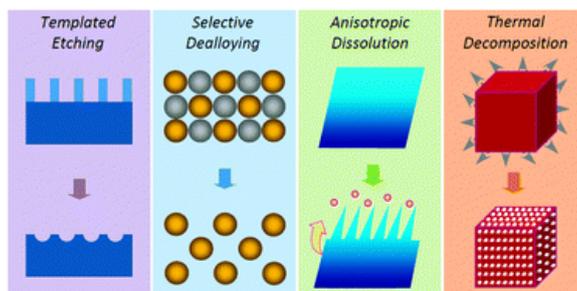
assessing the likely scope and limitations of a chemical reaction beyond the idealized reaction conditions initially reported. Using simple methods and common analytical techniques we demonstrate a rapid assessment of an established chemical reaction, and also propose a simplified analysis that may be reported alongside new synthetic methodology.

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- Chemical routes to top-down nanofabrication

Hai-Dong Yu, H.-D.; Regulacio, M. D.; Yea, E.; Han, M.-Y. *Chem. Soc. Rev.* **2013**, *42*, 6006-6018.

Abstract:



In fabricating materials at the nanometer scale, nanotechnologists typically employ two general strategies: bottom-up and top-down. While the bottom-up approach constructs nanomaterials from basic building blocks like atoms or molecules, the top-down approach produces nanostructures by deconstructing larger materials with the use of lithographic tools (*i.e.*, physical top-down) or through chemical-based processes (*i.e.*, chemical top-down). This tutorial review summarizes the various top-down nanofabrication methods, with great emphasis on the chemical routes that can generate nanoporous materials and ordered arrays of nanostructures with three-dimensional features. The chemical top-down routes that are discussed in detail include (1) templated etching, (2) selective dealloying, (3) anisotropic dissolution, and (4) thermal decomposition. These emerging nanofabrication tools open up new avenues in the creation of functional nanostructures with a wide array of promising applications.

- Recent progress in luminescent and colorimetric chemosensors for detection of thiols
Jung, H. S.; Chen, X; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2013**, *42*, 6019-6031.

Abstract:



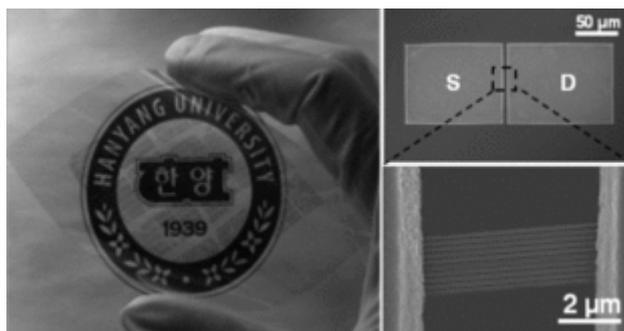
In the past few decades, the development of optical probes for thiols has attracted great attention because of the biological importance of the thiol-containing molecules such as cysteine (Cys), homocysteine (Hcy), and glutathione (GSH). This tutorial review focuses on various thiol detection methods based on luminescent or colorimetric spectrophotometry published during the period 2010–2012. The discussion covers a diversity of sensing mechanisms such as Michael addition,

cyclization with aldehydes, conjugate addition–cyclization, cleavage of sulfonamide and sulfonate esters, thiol–halogen nucleophilic substitution, disulfide exchange, native chemical ligation (NCL), metal complex-displace coordination, and nanomaterial-related and DNA-based chemosensors.

- High-Performance Air-Stable Single-Crystal Organic Nanowires Based on a New Indolocarbazole Derivative for Field-Effect Transistors

Park, K. S.; Salunkhe, S. M.; Lim, I.; Cho, C.-G.; Han, S.-H.; Sung, M. M. *Adv. Mater.* **2013**, *25*, 3351–3356.

Abstract:

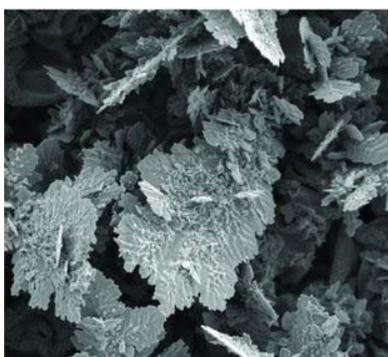


A new indolocarbazole derivative possessing an extended aromatic core and solubilizing long aliphatic chains effectively self-assembles and crystallizes within the nanoscale channels to form single-crystal nanowires via a direct printing method from an ink solution. Single-crystal organic nanowire transistor arrays based on the π -extended indolocarbazole derivative exhibit an excellent hole mobility of $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and outstanding environmental stability.

- Bench-Top Fabrication of Hierarchically Structured High-Surface-Area Electrodes

Gabardo, C. M.; Zhu, Y.; Soleymani, L.; Moran-Mirabal, J. M. *Adv. Funct. Mater.* **2013**, *23*, 3030–3039.

Abstract:

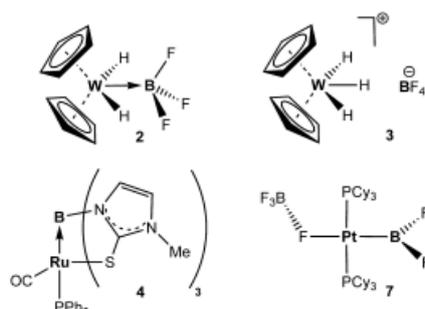


Fabrication of hierarchical materials, with highly optimized features from the millimeter to the nanometer scale, is crucial for applications in diverse areas including biosensing, energy storage, photovoltaics, and tissue engineering. In the past, complex material architectures have been achieved using a combination of top-down and bottom-up fabrication approaches. A remaining challenge, however, is the rapid, inexpensive, and simple fabrication of such materials systems using bench-top prototyping methods. To address this challenge, the properties of hierarchically structured electrodes are developed and investigated by combining three bench-top techniques: top-down electrode patterning using vinyl masks created by a computer-aided design (CAD)-driven cutter, thin film micro/nanostructuring using a shrinkable polymer substrate, and tunable electrodeposition of

conductive materials. By combining these methods, controllable electrode arrays are created with features in three distinct length scales: 40 μm to 1 mm, 50 nm to 10 μm , and 20 nm to 2 μm . The electrical and electrochemical properties of these electrodes are analyzed and it is demonstrated that they are excellent candidates for next generation low-cost electrochemical and electronic devices.

- Reactivity of Lewis Basic Platinum Complexes Towards Fluoroboranes
Bauer, J.; Braunschweig, H.; Dewhurst, R. D.; Radacki, K. *Chem. Eur. J.* **2013**, *27*, 8797-8805.

Abstract:

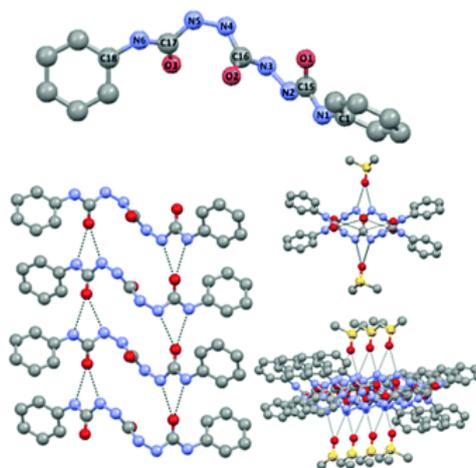


We herein report detailed investigations into the interaction of Lewis acidic fluoroboranes, for example BF_2Pf (Pf=perfluorophenyl) and $\text{BF}_2\text{Ar}^{\text{F}}$ (Ar^{F} =3,5-bis(trifluoromethyl)phenyl), with Lewis basic platinum complexes such as $[\text{Pt}(\text{PEt}_3)_3]$ and $[\text{Pt}(\text{PCy}_3)_2]$ (Cy=cyclohexyl). Two presumed Lewis adducts could be identified in solution and corresponding secondary products of these Lewis adducts were characterized in the solid state. Furthermore, the concept of frustrated Lewis pairs (FLP) was applied to the activation of ethene in the system $[\text{Pt}(\text{BF}_3)(\text{CH}_2\text{CH}_2)(\text{dcp})]$ (dcp=1,3-bis(dicyclohexylphosphino)propane; Pf=perfluorophenyl). Finally, DFT calculations were performed to determine the interaction between the platinum-centered Lewis bases and the boron-centered Lewis acids. Additionally, several possible mechanisms for the oxidative addition of the boranes BF_3 , BCl_3 , and $\text{BF}_2\text{Ar}^{\text{F}}$ to the model complex $[\text{Pt}(\text{PMe}_3)_2]$ are presented.

- The Tris-Urea Motif and Its Incorporation into Polydimethylsiloxane-Based Supramolecular Materials Presenting Self-Healing Features

Roy, N.; Buhler, E.; Lehn, J.-M. *Chem. Eur. J.* **2013**, *27*, 8814-8820.

Abstract:

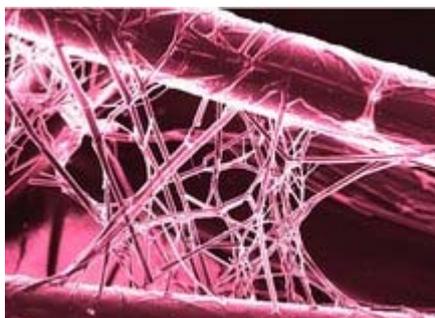


Materials of supramolecular nature have attracted much attention owing to their interesting features, such as self-reparability and material robustness, that are imparted by noncovalent interactions to synthetic materials. Among the various structures and synthetic methodologies that may be

considered for this purpose, the introduction of extensive arrays of multiple hydrogen bonds allows for the formation of supramolecular materials that may, in principle, present self-healing behavior. Hydrogen bonded networks implement dynamic noncovalent interactions. Suitable selection of structural units gives access to novel dynamic self-repairing materials by incrementing the number of hydrogen-bonding sites present within a molecular framework. Herein, we describe the formation of a tris-urea based motif giving access to six hydrogen-bonding sites, easily accessible through reaction of carbohydrazide with an isocyanate derivative. Extension towards the synthesis of multiply hydrogen-bonded supramolecular materials has been achieved by polycondensation of carbohydrazide with a bis-isocyanate component derived from poly-dimethylsiloxane chains. Such materials underwent self-repair at a mechanically cut surface. This approach gives access to a broad spectrum of materials of varying flexibility by appropriate selection of the bis-isocyanate component that forms the polymer backbone.

- Supramolecular Nanofiber Webs in Nonwoven Scaffolds as Potential Filter Media
Misslitz, H.; Kreger, K.; Schmidt, H-W. *Small* **2013**, *9*, 2053–2058.

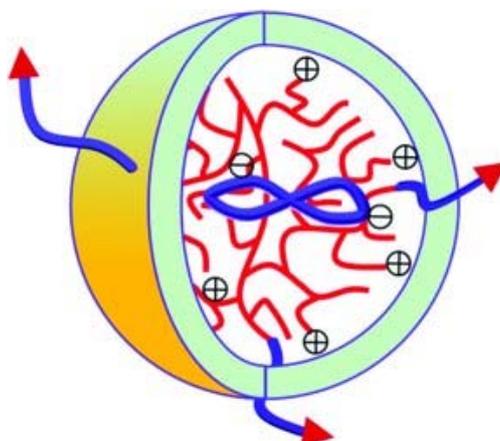
Abstract:



Microfiber–nanofiber composites are prepared by in situ formation of supramolecular nanofiber webs based on 1,3,5-benzenetricarboxamides in polymer nonwoven scaffolds. The supramolecular nanofibers are strongly fixed to nonwoven microfibers. These composites are sufficiently stable to be suited for air filtration applications.

- Nanoparticles for Gene Delivery
Tian, H.; Chen, J.; Chen, X. *Small* **2013**, *9*, 2034–2044.

Abstract:



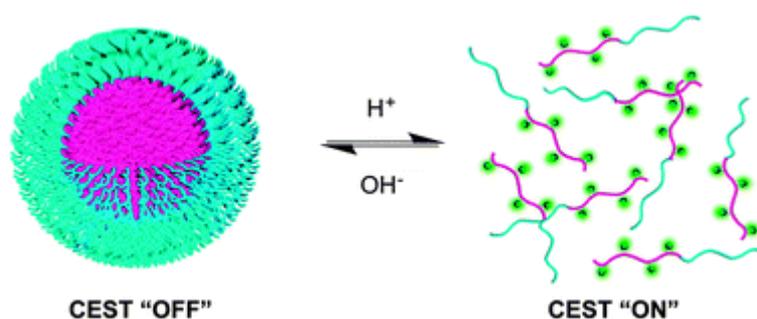
General concepts in the development of nanoparticle-based carriers for gene delivery systems are summarized. This concept highlights the current status and possible future directions of gene

delivery, with a particular emphasis on the clinical application of multifunctional nanocarriers on the combination of such properties as biodegradability, targetability, transfection ability, and stimuli sensitivity.

Nanocarriers are a new type of nonviral gene carriers, many of which have demonstrated a broad range of pharmacological and biological properties, such as being biodegradable in the body, stimulus-responsive towards the surrounding environment, and an ability to specifically targeting certain disease sites. By summarizing some main types of nanocarriers, this Concept considers the current status and possible future directions of the potential clinical applications of multifunctional nanocarriers, with primary attention on the combination of such properties as biodegradability, targetability, transfection ability, and stimuli sensitivity.

- A novel class of polymeric pH-responsive MRI CEST agents
Zhang, S.; Zhou, K.; Huang, G.; Takahashi, M.; Sherry, A. D.; Gao, J. *Chem. Commun.* **2013**, 49, 6418-6420.

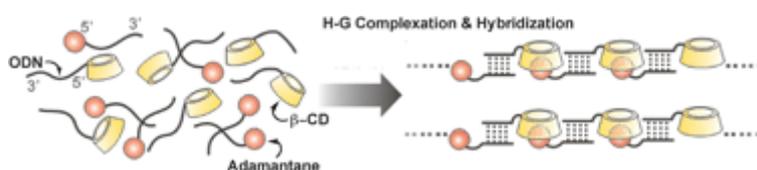
Abstract:



In this communication, we report that ionizable, tertiary amine-based block copolymers can be used as pH-responsive contrast agents for magnetic resonance imaging (MRI) through the chemical exchange saturation transfer (CEST) mechanism. The CEST signal is essentially “off” when the polymers form micelles near physiological pH but is activated to the “on” state when the micelles dissociate in an acidic environment.

- A supramolecular DNA self-assembly based on β -cyclodextrin–adamantane complexation as a bioorthogonal sticky end motif
Chiba, J.; Sakai, A.; Yamada, S.; Fujimoto, K.; Inouye, M. *Chem. Commun.* **2013**, 49, 6454-6456.

Abstract :



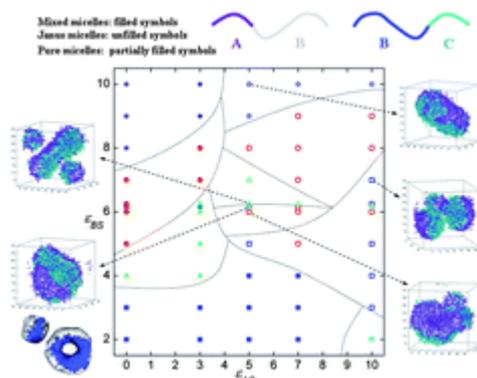
We propose linear end-to-end assemblies of short DNA duplexes based on β -cyclodextrin–adamantane complexation. The assembled duplexes exhibited increased T_m values compared with those of the corresponding natural hybrids. Competition experiments with external guest molecules showed a substantial decrease in T_m of the terminal modified duplexes, suggesting the viability of inter-duplex complexation.

- Janus-like spheres, disks, rings, cylinders, and vesicles from the self-assembly of mixture of

AB and BC diblock copolymers in A- and C-selective solvents
 Sheng, Y.; Yang, X.; Yan, N.; Zhu, Y. *Soft Matter* **2013**, *9*, 6254-6262.

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Abstract:

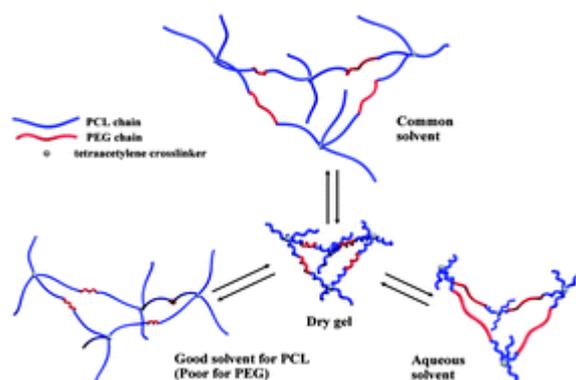


Janus particles with two different compartments have enormous potential as building blocks of hierarchically multifunctional nanomaterials. One of the most versatile and powerful methods to fabricate Janus micelles is through the solution-state self-assembly of block copolymers. In this study, we applied the Monte Carlo simulation to study the self-assembly of a AB/BC diblock copolymer mixture in A- and C-selective solvents. Our simulations predicted a variety of novel Janus micelles, which include Janus-like cylinders, lamellas, vesicles, and rings, all of which were self-assembled from amphiphilic A₄B₆/B₆C₄ copolymers. The effects of control parameters, which include the solvent quality for solvophobic B blocks (ϵ_{BS}) and the incompatibility between the solvophilic A and C blocks (ϵ_{AC}), on the formation of Janus micelles were examined, and a generic phase diagram in $\epsilon_{BS} \times \epsilon_{AC}$ was constructed. The phase diagram demonstrates that the micellar shape mainly depends on ϵ_{BS} , whereas the formation of the Janus architecture is controlled by ϵ_{AC} . Moreover, the formation pathways of the Janus lamella, vesicle, and ring were investigated and their formation mechanisms were investigated.

- Well-defined biodegradable amphiphilic conetworks

Yuan, Y.; Zhang, A.-K.; Ling, J.; Yin, L.-H.; Chen, Y.; Fu, G.-D. *Soft Matter* **2013**, *9*, 6309-6318.

Abstract:

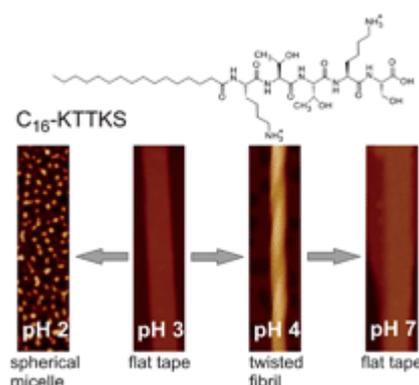


A series of amphiphilic conetworks (APCNs) with well-defined molecular structures were prepared *via* a copper-catalyzed 1,3-dipolar azide-alkyne cycloaddition (CuAAC) of tetrakis(2-propynyloxymethyl)methane (TMOP), diazide end-functionalized triblock copolymers of poly(ϵ -caprolactone) with poly(ethylene glycol) (N₃-PCL-PEG-PCL-N₃). The so-prepared APCNs exhibit unique properties of ordered nanophase separation of hydrophilic (HI) and hydrophobic (HO) phases, and a variable swelling capacity both in water and organic solvent. The morphology, surface properties and

thermal behavior of the APCNs were investigated by scanning electron microscopy (SEM), water contact angle (WCA), and differential scanning calorimetry (DSC), respectively. The physical properties of APCNs depended on the ratio of HI–HO, which can be regulated *via* precise synthesis of N₃-PCL-PEG-PCL-N₃. The analysis of an *in vitro* cell viability assay suggests that the APCNs have excellent biocompatibility. The prepared APCNs are excellent carriers for controlled drug release. The hydrophilic choline theophyllinate and hydrophobic 5-fluorouracil (5-FU) were loaded into the APCNs simultaneously as model drugs to study the release from APCNs. The well-controlled drug release is attributable to the well-defined molecular structure and tunable HI/HO composition of the APCNs.

- The effect of pH on the self-assembly of a collagen derived peptide amphiphile
Dehsorkhi, A.; Castelletto, V.; Hamley, I. W.; Adamcik, J.; Mezzenga, R. *Soft Matter* **2013**, *9*, 6033-6036.

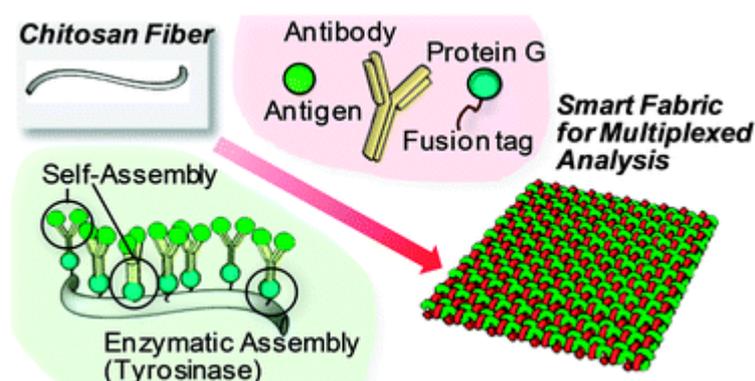
Abstract:



Transitions in nanostructure driven by pH are observed for a self-assembling peptide amphiphile (PA) with a cationic pentapeptide headgroup. At pH 3, the PA forms flat tape-like structures, while at pH 4 the PA assembles into twisted right handed structures. These twisted structures transform again to flat tape-like structures at pH 7. In complete contrast, spherical micelles are observed at pH 2. These changes in response to pH may be relevant to biological and pharmaceutical applications of this PA in skincare.

- Accessing biology's toolbox for the mesoscale biofabrication of soft matter
Payne, G. F.; Kim, E.; Cheng, Y.; Wu, H.-C.; Ghodssi, R.; Rubloff, G. W.; Raghavan, S. R.; Culver, J. N.; Bentley, W. E. *Soft Matter* **2013**, *9*, 6019-6032.

Abstract:



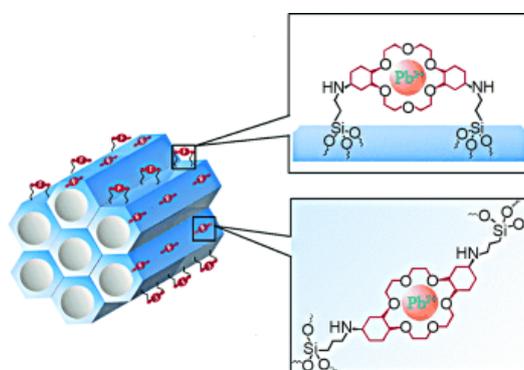
Biology is a master of mesoscale science, possessing unprecedented capabilities for fabricating components with nano-scale precision and then assembling them over a hierarchy of length scales.

Biology's fabrication prowess is well-recognized and there has been considerable effort to mimic these capabilities to create materials with diverse and multiple functions. In this review, we pose the question – why mimic, why not directly use the materials and mechanisms that biology provides to biofabricate functional materials? This question seems especially relevant when considering that many of the envisioned applications – from regenerative medicine to bioelectronics – involve biology. Here, we provide a sampling to illustrate how self-assembly, enzymatic-assembly and the emerging tools of modern biology can be enlisted to create functional soft matter. We envision that biofabrication will provide a biocompatible approach to mesoscale science and yield products that are safe, sustainable and potentially even edible.

- Site-Selective Functionalization of Periodic Mesoporous Organosilica (PMO) with Macrocyclic Host for Specific and Reversible Recognition of Heavy

Ye, G.; Leng, Y.; Bai, F.; Wei, J.; Wang, J.; Chen, J. *Chem. Asian J.* **2013**, *8*, 1482-1488.

Abstract:

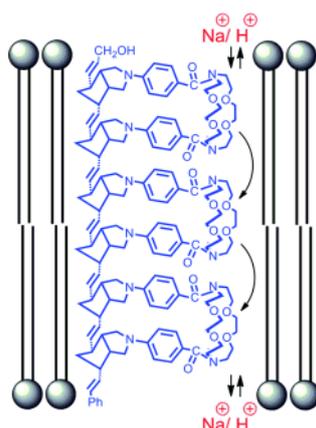


A novel kind of macrocyclic host-functionalized periodic mesoporous organosilica (PMO) with excellent and reversible recognition of PbII was developed. The macrocyclic host molecule cisdicyclohexano[18]crown-6, with strong affinity to PbII, was carefully modified as a bridged precursor to build the PMO material. To break down the limit of the functionalization degree for PMOs incorporated with large-sized moieties, a site-selective post-functionalization method was proposed to further decorate the external surface of the PMO material. The selective recognition ability of the upgraded PMO material towards PbII was remarkably enhanced without destroying the mesoporous ordering. Solidstate ^{13}C and ^{29}Si NMR spectroscopy, X-ray photoelectron spectroscopy (XPS), XRD, TEM, and nitrogen adsorption–desorption isotherm measurements were utilized for a full characterization of the structure, micromorphology, and surface properties. Reversible binding of PbII was realized in the binding–elution cycle experiments. The mechanism of the supramolecular interaction between the macrocyclic host and metal ion was discussed. The synthetic strategy can be considered a general way to optimize the properties of PMOs as binding materials for practical use while preserving the mesostructure.

- Oligonorborenes with Hammock-Like Crown Ether Pendants as Artificial Transmembrane Ion Channel

Lin, N.-T.; Xie, C.-Y.; Huang, S.-L.; Chen, C.-H.; Luh, T.-Y. *Chem. Asian J.* **2013**, *8*, 1436-1440.

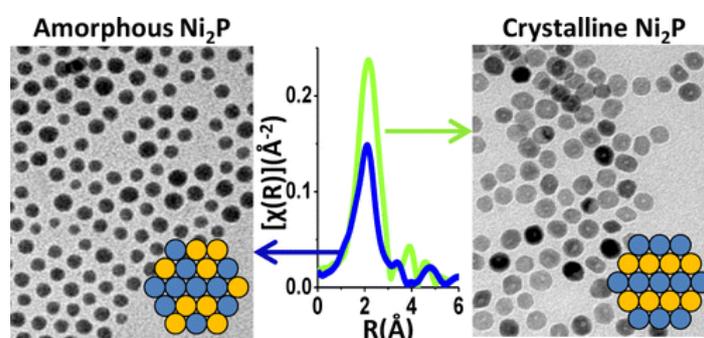
Abstract:



Trimeric oligonorborenes with hammock-like crown ether pendants **3 b** and **3 c** were selectively synthesized by cascade metathetical cyclopolymerization upon treatment with the first generation Grubbs catalyst. These crown-ether-containing oligonorborenes are impregnated in egg yolk phosphatidylcholine (EYPC) liposome as an artificial ion channel. The efficiency of the sodium ion transport properties has been examined. Oligomer **3 c** having a polar hydroxy end group exhibits the highest transport efficiency, which is comparable with the best efficiencies reported in literature. The orientation of the crown ether moieties in these oligomers may be critical for the ion transport properties.

- Defining Crystalline/Amorphous Phases of Nanoparticles through X-ray Absorption Spectroscopy and X-ray Diffraction: The Case of Nickel Phosphide
Moreau, L. M.; Ha, D.-H.; Zhang, H.; Hovden, R.; Muller, D. A.; Robinson, R. D. *Chem. Mater.* **2013**, 25, 2394-2403.

Abstract:

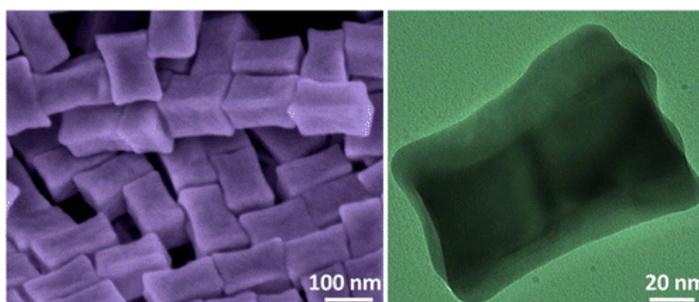


In this study we elucidate the structural distinctions between amorphous and crystalline Ni_2P nanoparticles synthesized using tri-*n*-octylphosphine (TOP), through X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and inductively coupled plasma (ICP). We determine the differences in their chemical and atomic structure, which have not been previously reported, yet are essential for understanding their potential as nanocatalysts. These structural characteristics are related to the corresponding nanoparticle magnetic properties analyzed by performing magnetic measurements. XAS results reveal a significant P concentration in the amorphous nanoparticle sample – placing the stoichiometry close to Ni_2P – despite XRD results that show only fcc Ni contributions. By comparing the long-range structural order from XRD to the short-range radial structure from EXAFS we conclude that both techniques are necessary to obtain a complete structural picture of amorphous and crystalline nanoparticle phases due to the limitations of XRD amorphous characterization. We find that phases are amorphous with respect to XRD when their offsets (deviations) from bulk interatomic

distances have a standard deviation as high as ~ 4.82 . Phases with lower standard deviation (e.g., 1.22), however, are detectable as crystalline through XRD. The possible presence of amorphous phases should be considered when using XRD alone for nanoparticle characterization. This is particularly important when highly reactive reagents such as TOP are used in synthesis. By characterizing amorphous nickel phosphide nanoparticles that have a comparable stoichiometry to Ni_2P , we confirm that TOP serves as a highly effective phosphorus source, even at temperatures as low as 230 °C. Unintended amorphous structure domains may significantly affect nanoparticle properties, and in turn, their functionality.

- Synthesis of Anisotropic Concave Gold Nanocuboids with Distinctive Plasmonic Properties
Huang, Y.; Wu, L.; Chen, X.; Bai, P.; Kim, D. H. *Chem. Mater.* **2013**, *25*, 2470-2475.

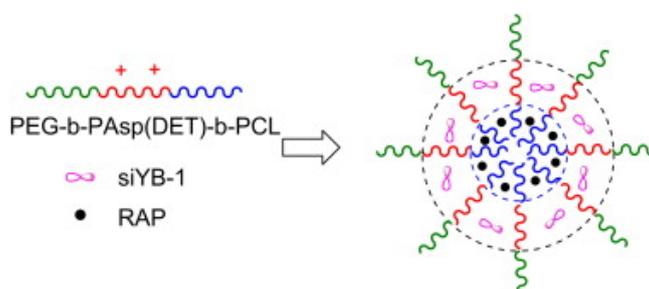
Abstract:



Gold nanoparticles have attracted considerable attention owing to their appealing plasmonic properties that have found applications in sensing, imaging, and energy harvesting. In the present article, we report the synthesis of anisotropic concave Au nanocuboids using a seeded growth method controlled by a seed concentration. Unlike conventional nonconcave counterparts which typically present two fundamental plasmonic modes (transverse and longitudinal modes), our experimental measurements and theoretical analysis show that the anisotropic concave Au nanocuboid has three plasmonic resonances. Theoretical calculations based on a finite element method confirm that the third resonance is a transverse “edge” mode, which is enhanced by the sharpened edges of the concave surfaces. This third resonance is found to be separated from the conventional broad transverse mode band. Because of the separation of the resonance mode, the quality-factor of the original transverse mode shows nearly a 3-fold enhancement.

- Trilayer micelles for combination delivery of rapamycin and siRNA targeting Y-box binding protein-1 (siYB-1)
Zeng, S.; Xiong, M. P. *Biomaterials* **2013**, *34*, 6882-6892.

Abstract:



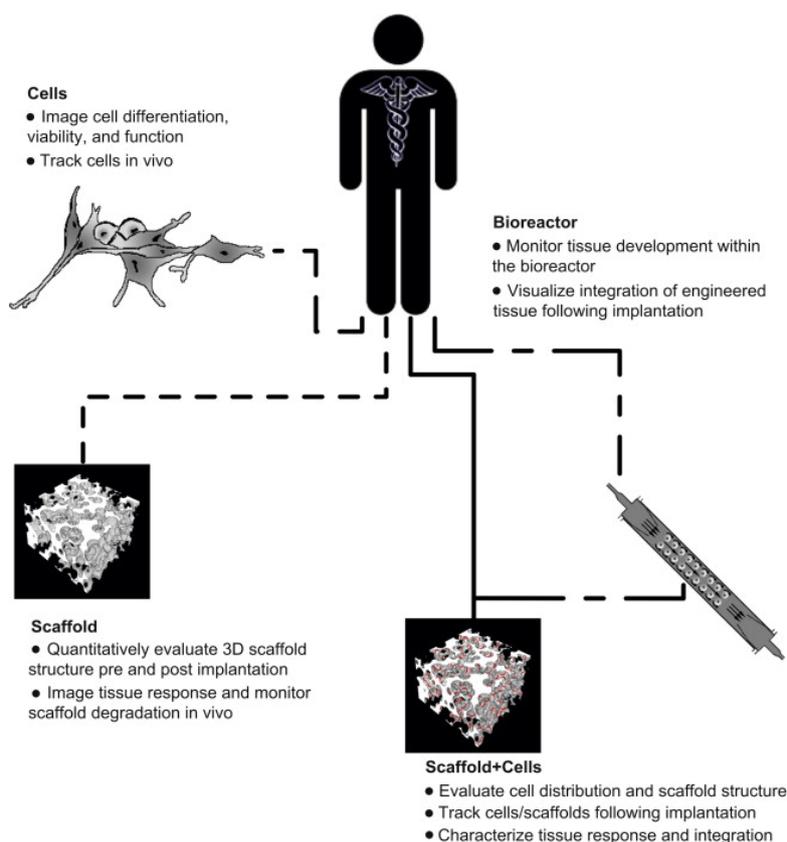
A three layer (trilayer) polymeric micelle system based on the self-association of the triblock polymer poly(ethylene glycol)-b-poly{N-[N-(2-aminoethyl)-2-aminoethyl] aspartamide}-b-poly(ϵ -caprolactone)

(PEG-b-PAsp(DET)-b-PCL) has been synthesized and investigated for combination delivery of rapamycin (RAP) and siRNA targeting Y-box binding protein-1 (siYB-1). The trilayer micelle is composed of (a) a hydrophilic poly(ethylene glycol) (PEG) block constituting the outer layer to improve pharmacokinetics, (b) an intermediate compartment composed of the cationic poly{2-[(2-aminoethyl)amino] ethyl aspartamide} (PAsp(DET)) segment for interacting with siYB-1, and (c) an inner hydrophobic poly(ϵ -caprolactone) (PCL) compartment for encapsulation of RAP. A major advantage of this system is biocompatibility since PEG and PCL are both approved by the FDA, and PAsp(DET) is a non-toxic pH responsive cationic poly(amino acid)-based polymer. In this study, it has been shown that PCL can encapsulate RAP with high loading efficiencies, and PAsp(DET) can successfully interact with siRNA for efficient transfection/knockdown with negligible cytotoxicity. The enhanced therapeutic efficacy of RAP/siYB-1 micelles was demonstrated in cell cultures and in a PC3 xenograft nude mouse model of human prostate cancer. Herein, we demonstrate that trilayer micelles are a promising approach to improve the simultaneous delivery of combination siRNA/drug therapies.

- Imaging challenges in biomaterials and tissue engineering

Appel, A. A.; Anastasio, M. A.; Larson, J. C.; Brey, E. M. *Biomaterials* **2013**, *34*, 6615-6630.

Abstract:



Biomaterials are employed in the fields of tissue engineering and regenerative medicine (TERM) in order to enhance the regeneration or replacement of tissue function and/or structure. The unique environments resulting from the presence of biomaterials, cells, and tissues result in distinct challenges in regards to monitoring and assessing the results of these interventions. Imaging technologies for three-dimensional (3D) analysis have been identified as a strategic priority in TERM research. Traditionally, histological and immunohistochemical techniques have been used to evaluate

engineered tissues. However, these methods do not allow for an accurate volume assessment, are invasive, and do not provide information on functional status. Imaging techniques are needed that enable non-destructive, longitudinal, quantitative, and three-dimensional analysis of TERM strategies. This review focuses on evaluating the application of available imaging modalities for assessment of biomaterials and tissue in TERM applications. Included is a discussion of limitations of these techniques and identification of areas for further development.