Double and Single Network Phases in Polystyrene-block-poly(I-lactide) Diblock Copolymers. Wang, X.-B.; Lo, T.-Y.; Hsueh, H.-Y.; Ho, R.-M. *Macromolecules* 2013, 46, 2997-3004. <u>Abstract:</u>



Here, the phase behaviors of polystyrene-block-poly(I-lactide) (PS–PLLA) diblock copolymers are studied, and network phases can be found. In addition to conventional double gyroid phase with double networks, a single network phase (an Fddd phase with orthorhombic network) can be found, as evidenced by small-angle X-ray scattering and transmission electron microscopy (TEM). The single network texture with trivalent connectors of the Fddd can be directly visualized by using 3D TEM (i.e., electron tomography), and the observation under polarized light microscopy shows its birefringence character. The formation of stable Fddd is attributed to intrinsic inhomogeneity in the chain conformations of the chiral block (i.e., PLLA). Subsequently, nanoporous PS with continuous nanochannel networks can be obtained by hydrolysis of the PLLA block in the PS–PLLA and then used as a template for sol–gel reaction of tetraethyl orthosilicate. Consequently, nanoporous SiO<sub>2</sub> with free-standing, well-defined network texture can be fabricated after removal of the PS template to give an open-cell porous ceramic material with high specific surface area (as high as 1170 m<sup>2</sup>/g) due to its nanostructured texture and high porosity.

 Light-Responsive Polystyrene Films Doped with Tailored Heteroaromatic-Based Fluorophores. Minei, P.; Battisti, A.; Barondi, S.; Lessi, M.; Bellina, F.; Ruggeri, G.; Pucci, A. ACS Macro Lett. 2013, 2, 317-321.

Abstract:



We describe a simple but effective strategy for imparting light-responsive peculiarity to polystyrene films. A pH-sensitive fluorescent dye having the electron-poor pyridine nucleus as a key structural feature was synthesized and dispersed at low loadings (0.2–0.5 wt %) in a PS matrix. Once light irradiation in the near-UV range was sent to PS/dye films, PS photooxidation likely occurred at the film surface with the formation of carboxylic compounds. These species locally promoted dye protonation, thus, yielding a clear change of the film emission from blue to green. This study opens the door to a wide range of light-responsive materials from easily accessible polymers, enabling the use of UV light as an effective trigger for smart materials and devices.

<sup>1</sup> 

 Self-assembly of a model amphiphilic oligopeptide incorporating an arginine headgroup Hamley, I. W.; Dehsorkhi, A.; Castelletto, V.; Seitsonen, J.; Ruokolainen, J.; latrou, H.Soft 2 Matter 2013, 9, 4794-4801.





The self-assembly in aqueous solution of the alanine-rich peptide  $A_{12}R_2$  containing twelve alanine residues and two arginine residues has been investigated. This oligomeric peptide was synthesized *via* NCA-polymerization methods. The surfactant-like peptide is found *via* FTIR to form antiparallel dimers which aggregate into twisted fibrils, as revealed by cryogenic-transmission electron microscopy. The fibril substructure is probed *via* detailed X-ray scattering experiments, and are uniquely comprised of twisted tapes only 5 nm wide, set by the width of the antiparallel  $A_{12}R_2$  dimers. The packing of the alanine residues leads to distinct " $\beta$ -sheet" spacings compared to those for amyloid-forming peptides. For this peptide,  $\beta$ -sheet structure coexists with some  $\alpha$ -helical content. These ultrafine amyloid fibrils present arginine at high density on their surfaces, and this may lead to applications in nanobiotechnology.

 Cross-linked supramolecular polymer networks with responsive and elastic gel properties via host-guest complexation: controlled release of squaraine dyes Zeng, F.; Shen, Y.; Chen, C.-F. *Soft Matter* **2013**, *9*, 4875-4882.
<u>Abstract:</u>



Triptycene-derived macrotricyclic polyether was proved to be an efficient "molecular glue" for crosslinking the copolymer containing dibenzylammonium salts to form supramolecular polymer networks *via* host–guest complexation, which was evidenced by <sup>1</sup>H NMR spectroscopy, solution viscometry, and formation of transparent and elastic supramolecular polymer gels. Interestingly, a well-defined porous structure of the supramolecular polymer gel could be observed at the fully cross-linked density, and its mechanical properties could be modulated by the amount of the macrotricyclic host added to the system. Moreover, the supramolecular polymer gel showed acid/base- and thermo-induced reversible gel–sol transitions. Additionally, the supramolecular polymer gel could also be employed for the encapsulation and controllable release of squaraine dyes, which might find 3

The Cation-π Interaction
Dougherty, D. A. Acc. Chem. Res. 2013, 46, 885–893.
<u>Abstract:</u>



The chemistry community now recognizes the cation– $\pi$  interaction as a major force for molecular recognition, joining the hydrophobic effect, the hydrogen bond, and the ion pair in determining macromolecular structure and drug–receptor interactions. This *Account* provides the author's perspective on the intellectual origins and fundamental nature of the cation– $\pi$  interaction.

Early studies on cyclophanes established that water-soluble, cationic molecules would forego aqueous solvation to enter a hydrophobic cavity if that cavity was lined with  $\pi$  systems. Important gas phase studies established the fundamental nature of the cation- $\pi$  interaction. The strength of the cation- $\pi$  interaction (Li<sup>+</sup> binds to benzene with 38 kcal/mol of binding energy; NH<sub>4</sub><sup>+</sup> with 19 kcal/mol) distinguishes it from the weaker polar- $\pi$  interactions observed in the benzene dimer or water-benzene complexes. In addition to the substantial intrinsic strength of the cation- $\pi$  interaction in gas phase studies, the cation- $\pi$  interaction remains energetically significant in aqueous media and under biological conditions. Many studies have shown that cation- $\pi$  interactions can enhance binding energies by 2–5 kcal/mol, making them competitive with hydrogen bonds and ion pairs in drug-receptor and protein-protein interactions.

As with other noncovalent interactions involving aromatic systems, the cation– $\pi$  interaction includes a substantial electrostatic component. The six (four)  $C^{\delta-}-H^{\delta+}$  bond dipoles of a molecule like benzene (ethylene) combine to produce a region of negative electrostatic potential on the face of the  $\pi$ system. Simple electrostatics facilitate a natural attraction of cations to the surface. The trend for (gas phase) binding energies is Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> > Rb<sup>+</sup>: as the ion gets larger the charge is dispersed over a larger sphere and binding interactions weaken, a classical electrostatic effect. On other hand, polarizability does not define these interactions. Cyclohexane is more polarizable than benzene but a decidedly poorer cation binder.

Many studies have documented cation– $\pi$  interactions in protein structures, where lysine or arginine side chains interact with phenylalanine, tyrosine, or tryptophan. In addition, countless studies have established the importance of the cation– $\pi$  interaction in a range of biological processes. Our work has focused on molecular neurobiology, and we have shown that neurotransmitters generally use a cation– $\pi$  interaction to bind to their receptors. We have also shown that many drug–receptor interactions involve cation– $\pi$  interactions. A cation– $\pi$  interaction plays a critical role in the binding of nicotine to ACh receptors in the brain, an especially significant case. Other researchers have

4

established important cation- $\pi$  interactions in the recognition of the "histone code," in terpene biosynthesis, in chemical catalysis, and in many other systems.

 On the Importance and Origin of Aromatic Interactions in Chemistry and Biodisciplines Riley, K. E.; Hobza, P. Acc. Chem. Res. 2013, 46, 927–936.
<u>Abstract:</u>



Aromatic systems contain both  $\sigma$ - and  $\pi$ -electrons, which in turn constitute  $\sigma$ - and  $\pi$ -molecular orbitals (MOs). In discussing the properties of these systems, researchers typically refer to the highest occupied and lowest unoccupied MOs, which are  $\pi$  MOs. The characteristic properties of aromatic systems, such as their low ionization potentials and electron affinities, high polarizabilities and stabilities, and small band gaps (in spectroscopy called the N  $\rightarrow$  V<sub>1</sub> space), can easily be explained based on their electronic structure. These one-electron properties point to characteristic features of how aromatic systems interact with each other.

Unlike hydrogen bonding systems, which primarily interact through electrostatic forces, complexes containing aromatic systems, especially aromatic stacked pairs, are predominantly stabilized by dispersion attraction. The stabilization energy in the benzene dimer is rather small (~2.5 kcal/mol) but strengthens with heteroatom substitution. The stacked interaction of aromatic nucleic acid bases is greater than 10 kcal/mol, and for the most stable stacked pair, guanine and cytosine, it reaches approximately 17 kcal/mol. Although these values do not equal the planar H-bonded interactions of these bases (~29 kcal/mol), stacking in DNA is more frequent than H-bonding and, unlike H-bonding, is not significantly weakened when passing from the gas phase to a water environment.

Consequently, the stacking of aromatic systems represents the leading stabilization energy contribution in biomacromolecules and in related nanosystems. Therefore stacking (dispersion) interactions predominantly determine the double helical structure of DNA, which underlies its storage and transfer of genetic information. Similarly, dispersion is the dominant contributor to attractive interactions involving aromatic amino acids within the hydrophobic core of a protein, which is critical for folding.

Therefore, understanding the nature of aromatic interactions, which depend greatly on quantum mechanical (QM) calculations, is of key importance in biomolecular science. This Account shows that accurate binding energies for aromatic complexes should be based on computations made at the (estimated) CCSD(T)/complete basis set limit (CBS) level of theory. This method is the least computationally intensive one that can give accurate stabilization energies for all common classes of noncovalent interactions (aromatic–aromatic, H-bonding, ionic, halogen bonding, charge-transfer, etc.). These results allow for direct comparison of binding energies between different interaction types. Conclusions based on lower-level QM calculations should be considered with care.

• Significant Expansion of the Fluorescent Protein Chromophore through the Genetic

Incorporation of a Metal-Chelating Unnatural Amino Acid

Liu, X.; Li, J.; Hu, C.; Zhou, Q.; Zhang, W.; Hu, M.; Zhou, J.; Wang, J. *Angew. Chem. Int. Ed.* **5 2013**, *52*, 4805–4809.

Abstract:



Caught red-shifted: A novel metal-chelating unnatural amino acid with an 8-hydroxyquinoline group (HqAla) can be enzymatically incorporated into GFP (see scheme). Substituting a Tyr residue in the chromophore of FPs with HqAla results in significantly red-shifted excitation and emission maxima. The crystal structure of superfolder GFP bearing HqAla in its chromophore shows the structural basis for these red shifts.

A Chemical Probe for Lysine Malonylation
Bao, X.; Zhao, Q.; Yang, T.; Fung, Y. M. E.; Li, X. D. Angew. Chem. Int. Ed. 2013, 52, 4883–4886.
<u>Abstract:</u>



Tag! You're it! MalAM-yne is a chemical reporter for malonylation of lysines within proteins (see scheme), a newly identified posttranslational modification. MalAM-yne is cell-permeable and metabolically incorporated into proteins in living cells. Subsequent bioorthogonal tag conjugation allows the fluorescent visualization of cellular malonylation and profiling of malonylated proteins.

 Nanobatteries in redox-based resistive switches require extension of memristor theory Valov, I.; Linn, E.; Tappertzhofen, S.; Schmelzer, S.; van den Hurk, J.; Lentz, F.; Waser, R. *Nature Commun.* 2013, *4*, 1771.

Abstract:



Redox-based nanoionic resistive memory cells are one of the most promising emerging nanodevices for future information technology with applications for memory, logic and neuromorphic computing. 6 Recently, the serendipitous discovery of the link between redox-based nanoionic-resistive memory cells and memristors and memristive devices has further intensified the research in this field. Here we show on both a theoretical and an experimental level that nanoionic-type memristive elements are inherently controlled by non-equilibrium states resulting in a nanobattery. As a result, the memristor theory must be extended to fit the observed non-zero-crossing I–V characteristics. The initial electromotive force of the nanobattery depends on the chemistry and the transport properties of the materials system but can also be introduced during redox-based nanoionic-resistive memory cell operations. The emf has a strong impact on the dynamic behaviour of nanoscale memories, and thus, its control is one of the key factors for future device development and accurate modelling.

• An autonomous photosynthetic device in which all charge carriers derive from surface plasmons

Mubeen, S.; Lee, J.; Singh, N.; Krämer, S.; Stucky, G. D.; Moskovits, M. Nature Nano. 2013, 8, 247–251.

Abstract:



Solar conversion to electricity or to fuels based on electron-hole pair production in semiconductors is a highly evolved scientific and commercial enterprise. Recently, it has been posited that charge carriers either directly transferred from the plasmonic structure to a neighbouring semiconductor (such as TiO<sub>2</sub>) or to a photocatalyst, or induced by energy transfer in a neighbouring medium, could augment photoconversion processes, potentially leading to an entire new paradigm in harvesting photons for practical use. The strong dependence of the wavelength at which the local surface plasmon can be excited on the nanostructure makes it possible, in principle, to design plasmonic devices that can harvest photons over the entire solar spectrum and beyond. So far, however, most such systems show rather small photocatalytic activity in the visible as compared with the ultraviolet. Here, we report an efficient, autonomous solar water-splitting device based on a gold nanorod array in which essentially all charge carriers involved in the oxidation and reduction steps arise from the hot electrons resulting from the excitation of surface plasmons in the nanostructured gold. Each nanorod functions without external wiring, producing  $5 \times 1013$  H<sub>2</sub> molecules per cm<sup>2</sup> per s under 1 sun illumination (AM 1.5 and 100 mW cm<sup>-2</sup>), with unprecedented long-term operational stability.

Direct Evidence of a Dinuclear Copper Intermediate in Cu(I)-Catalyzed Azide-Alkyne Cycloadditions
Worrell, B. T.; Malik, J. A.; Fokin, V. V. Science 2013, 340, 457-460.
<u>Abstract:</u>



Copper(I)-catalyzed azide-alkyne cycloaddition has become a commonly employed method for the synthesis of complex molecular architectures under challenging conditions. Despite the widespread use of copper-catalyzed cycloaddition reactions, the mechanism of these processes has remained difficult to establish due to the involvement of multiple equilibria between several reactive intermediates. Real-time monitoring of a representative cycloaddition process via heat-flow reaction calorimetry revealed that monomeric copper acetylide complexes are not reactive toward organic azides unless an exogenous copper catalyst is added. Furthermore, crossover experiments with an isotopically enriched exogenous copper source illustrated the stepwise nature of the carbon–nitrogen bond-forming events and the equivalence of the two copper atoms within the cycloaddition steps.

Protein chemical synthesis by serine and threonine ligation
Zhang, Y.; Xu, C.; Lam, H. Y.; Lee, C. L.; Li, X. Proc. Natl. Acad. Sci. USA 2013, 110, 6657-6662.
<u>Abstract:</u>



An efficient method has been developed for the salicylaldehyde ester-mediated ligation of unprotected peptides at serine (Ser) or threonine (Thr) residues. The utility of this peptide ligation approach has been demonstrated through the convergent syntheses of two therapeutic peptides– ovine-corticoliberin and Forteo–and the human erythrocyte acylphosphatase protein (~11 kDa). The requisite peptide salicylaldehyde ester precursor is prepared in an epimerization-free manner via Fmoc–solid-phase peptide synthesis.

• N-Type Self-Assembled Monolayer Field-Effect Transistors and Complementary Inverters Ringk, A.; Li, X.; Gholamrezaie, F.; Smits, E. C. P.; Neuhold, A.; Moser, A.; Van der Marel, C.; Gelinck, G. H.; Resel, R.; de Leeuw, D. M.; Strohriegl, P. *Adv. Mater.* **2013**, *23*, 2016–2023.

## Abstract:



Highly reproducible n-type self-assembled monolayer field-effect transistors (SAMFETs) based on a perylene derivative are reported. Electron mobilities of  $1.5 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> and on/off current ratios up to  $10^{5}$  are obtained. By implementing n-type and p-type transistors in one device, a complimentary inverter based solely on SAMFETs is demonstrated for the first time.

 Nanostructured Crystalline Comb Polymer of Perylenebisimide by Directed Self-Assembly: Poly(4-vinylpyridine)-pentadecylphenol Perylenebisimide Narayan, R.; Kumar, P.; Narayan, K. S.; Asha, S. K. Adv. Funct. Mater. 2013, 23, 2033–2043. <u>Abstract:</u>



**Supramolecular complex formation of an asymmetrical perylenebisimide (PDP-UPBI)** with poly(4-vinylpyridine) (P4VP) via non-covalent specific interaction such as hydrogen bonding is described. The complexation results in the formation of uniform lamellar structures in the domain range of 5–10 nm.

• The Quest for Shape Control: A History of Gold Nanorod Synthesis Lohse, S. E.; Murphy, C. J. *Chem. Mater.* **2013**, *25*, 1250-1261. <u>Abstract:</u>



The development of facile seeded growth syntheses for anisotropic gold nanoparticles (particularly

9

gold nanorods) has spurred an interest in their optical properties and applications. The development of the first seeded growth synthesis for gold nanorods in 2001 was a transformative event, providing the first simple, convenient wet chemistry route to these nanomaterials. Over the past decade, the original seeded growth procedure has been the subject of further modifications that have continuously expanded researchers' access to anisotropic gold nanoparticles. Recent modifications to the synthesis have improved synthetic control over gold nanorod aspect ratio, increased synthesis up to the gram scale, and provided the opportunity to tightly control the absolute dimensions of AuNRs. Despite these advances, the mechanism of gold nanorod growth in this synthesis remains poorly understood. Recent investigations into gold nanorod growth mechanisms have revealed the process to be unexpectedly complex, suggesting that many different reagents interact synergistically to promote shape control, and that growth of the AuNR core may proceed by complex processes, such as stochastic nanorod growth. Nevertheless, the advent of new in situ characterization techniques promises to shortly reveal new insights into gold nanorod core growth, and may inform further significant modifications, improving the efficiency and versatility of seeded growth synthesis. In this review, we recount the history of the seeded growth synthesis for gold nanorods, examine the impact of recent advances in this synthesis, and current investigations into the mechanism of gold nanorod growth.

 Chemical Mechanisms of Semiconductor Nanocrystal Synthesis Sowers, K. L.; Swartz, B.; Krauss, T. D. *Chem. Mater.* 2013, *25*, 1351-1362.
<u>Abstract:</u>



Semiconductor nanocrystal quantum dots (QDs) have been the subject of much interest for fundamental and applied studies. The synthesis of QDs has developed over the past 30 years such that production of monodisperse, photostable QDs with a near-exact size and shape are readily achievable. However, an understanding of the chemical reaction mechanism behind the synthesis of QDs has lagged the ability to synthesize high-quality nanoparticles. This review will discuss recent studies of QD synthetic mechanisms that have been proposed for metal-chalcogenide (ME) semiconductor QDs, particularly CdE and PbE. Although the focus here will be on the initial metal-chalcogenide bond formation, we will also discuss growth models for QDs as well as attempt to provide a future outlook for how understanding reaction mechanism can be leveraged to make improved QDs with easily tailored properties.

 Charge Transport in Photoswitchable Dimethyldihydropyrene-Type Single-Molecule Junctions Roldan, D.; Kaliginedi, V.; Cobo, S.; Kolivoska, V.; Bucher, C.; Hong, W.; Royal, G.; Wandlowski, T. J. Am. Chem. Soc. 2013, 135, 5974–5977. <u>Abstract:</u>



The conductance properties of a photoswitchable dimethyldihydropyrene (DHP) derivative have been investigated for the first time in single-molecule junctions using the mechanically controllable break junction technique. We demonstrate that the reversible structure changes induced by isomerization of a single bispyridine-substituted DHP molecule are correlated with a large drop of the conductance value. We found a very high ON/OFF ratio (>10<sup>4</sup>) and an excellent reversibility of conductance switching.

 The Copper Active Site of CBM33 Polysaccharide Oxygenases Hemsworth, G. R.; Taylor, E. J.; Kim, R. Q.; Gregory, R. C.; Lewis, S. J.; Turkenburg, J. P.; Parkin, A.; Davies, G. J.; Walton, P. H. J. Am. Chem. Soc. 2013, 135, 6069–6077. <u>Abstract:</u>



The capacity of metal-dependent fungal and bacterial polysaccharide oxygenases, termed GH61 and CBM33, respectively, to potentiate the enzymatic degradation of cellulose opens new possibilities for the conversion of recalcitrant biomass to biofuels. GH61s have already been shown to be unique metalloenzymes containing an active site with a mononuclear copper ion coordinated by two histidines, one of which is an unusual τ-N-methylated N-terminal histidine. We now report the structural and spectroscopic characterization of the corresponding copper CBM33 enzymes. CBM33 binds copper with high affinity at a mononuclear site, significantly stabilizing the enzyme. X-band EPR spectroscopy of Cu(II)-CBM33 shows a mononuclear type 2 copper site with the copper ion in a distorted axial coordination sphere, into which azide will coordinate as evidenced by the concomitant formation of a new absorption band in the UV/vis spectrum at 390 nm. The enzyme's three-dimensional structure contains copper, which has been photoreduced to Cu(I) by the incident X-rays, confirmed by X-ray absorption/fluorescence studies of both aqueous solution and intact crystals of Cu-CBM33. The single copper(I) ion is ligated in a T-shaped configuration by three nitrogen atoms from two histidine side chains and the amino terminus, similar to the endogenous copper coordination geometry found in fungal GH61.

 Silver Nanoassemblies Constructed from Boranephosphonate DNA Roy, S.; Olesiak, M.; Shang, S.; Caruthers, M. H. J. Am. Chem. Soc., 2013, 135, 6234–6241. <u>Abstract:</u>



Spatially selective deposition of metal onto complex DNA assemblies is a promising approach for the preparation of metallic nanostructures with features that are smaller than what can be produced by top-down lithographic techniques. We have recently reported the ability of 2'-deoxyoligonucleotides containing boranephosphonate linkages (bpDNA) to reduce AuCl<sup>4–</sup>, Ag<sup>+</sup>, and PtCl<sub>4</sub><sup>2–</sup> ions to the corresponding nanoparticles. Here we demonstrate incorporation of bpDNA oligomers into a two-dimensional DNA array comprised of tiles containing double crossover junctions. We further demonstrate the site-specific deposition of metallic silver onto this DNA structure which generates well-defined and preprogrammed arrays of silver nanoparticles. With this approach the size of the metallic features that can be produced is limited only by the underlying DNA template. These advances were enabled due to a new method for synthesizing bpDNA that uses a silyl protecting group on the DNA nucleobases during the solid-phase 2'-deoxyoligonucleotide synthesis.

• Synthesis and recognition studies with a ditopic, photoswitchable deep cavitand Busseron, E.; Lux, J.; Degardina, M.; Rebek, J. *Chem. Commun.* **2013**, *49*, 4842-4844. <u>Abstract:</u>



We describe the synthesis and photochemical behavior of open-ended container modules connected by a 4,4'-azobiphenyl spacer. Both trans and cis azo configurations of the host can be accessed and their binding of guest molecules was characterized by NMR methods.

 Peptide self-assembly driven by oxo-ester mediated native chemical ligation Rasale, D. B.; Maity, I.; Kondaa, M.; Das, A. K. *Chem. Commun.* 2013, 49, 4815-4817. <u>Abstract:</u>



We use the oxo-ester mediated native chemical ligation (NCL) reaction to generate a peptide selfassembly process to make supramolecular nanofibers and self-supporting gels. 12

• Carbon Nanotube Photoelectronic and Photovoltaic Devices and their Applications in Infrared Detection

Yang, L.; Wang, S.; Zeng, Q.; Zhang, Z.; Peng, L-M. *Small* **2013**, *9*, 1225–1236. <u>Abstract:</u>



Semiconducting carbon nanotubes (CNTs) are direct bandgap materials with outstanding electronic and optoelectronic properties and have been investigated for various electronic and optoelectronic device applications, such as light-emitting diodes, photodetectors and photovoltaic cells. Here, a brief review of the various types of CNT diodes is presented, with a focus on one particular type of CNT diodes fabricated via a doping-free process. Their application for constructing high-performance optoelectronic and photovoltaic devices is also discussed, as well as the newly discovered photovoltage multiplication effect in CNTs and its application in improving the efficiency of CNTbased infrared detector.

 Photocatalytic Engineering of Single-Walled Carbon Nanotubes: From Metal-to-Semiconductor Conversion to Cutting and Patterning Nie, Y.; Zhang, L.; Wu, D.; Chen, Y.; Zhang, G.; Xie, Q.; Liu, Z. Small 2013, 9, 1336–1341. <u>Abstract:</u>



With a TiO<sub>2</sub>-based photocatalytic approach, both an arbitrary geometry tailoring of single-walled carbon nanotubes (SWCNTs) on various substrates and the conversion of metallic to semiconducting SWCNTs are demonstrated. Taking advantage of the selectivity on the diameter and metallicity of SWCNTs, 100% depletable SWCNT-based field-effect transistors are achieved, with lon/loff improvements up to five orders of magnitude.

• DNA origami technology for biomaterials applications

Endo, M.; Yang, Y.; Hiroshi Sugiyama, H. *Biomater. Sci.* **2013**, *1*, 347-360. <u>Abstract:</u>



DNA origami is an emerging technology for designing and constructing defined multidimensional nanostructures. This technology is now expanding to materials science. This article introduces the basics of DNA origami, the design of various two-dimensional and three-dimensional DNA origami structures, and the programmed assembly of origami structures. DNA origami has unique properties, such as an addressable surface, which enables selective functionalization with biomolecules and nanomaterials. The origami can also be combined with top-down nanotechnology, such as placement on a fabricated substrate. The technology is also applied to single-molecule imaging and analysis systems constructed on designed DNA origami structures. Furthermore, DNA mechanical nanodevices working on DNA origami have been realized, and cell-oriented applications are now in progress. DNA origami technology has practical potential in various research fields.

 Designer D-form self-assembling peptide nanofiber scaffolds for 3-dimensional cell cultures Luo, Z.; Yue, Y.; Zhang, Y.; Yuan, X.; Gong, J.; Wang, L.; He, B.; Liu, Z.; Sun, Y.; Liu, J.; Hu, M.; Zheng, J. *Biomaterials* 2013, *34*, 4902-4913.
<u>Abstract:</u>



Traditional 2-D cell cultures have many limitations because they do not truly mimic the natural environment. In order to fully understand the *in vivo* 3-D environment, it is crucial to develop a biomimetic 3-D culture system. Recently progress toward 3-D tissue cell cultures has been gradually made by addressing many critical issues including the microenvironment, gradient diffusion and apoptosis. Here we report a D-form self-assembly peptide system that provides insight into the relationships between nanofiber scaffolds and cell behaviors in 3-D cell cultures. We observed the peptide secondary structures response to ions and confirmed that their participation increases mechanical force rapidly. We also showed the enzymes attachment to nanofibers, investigated

scaffolds to form 3-D microenvironment and described a modified protocol for 3-D cell culture D-form self-assembly peptide. Using this protocol, we showed cell behavior in the D-form peptide with high cell viability and low-level cell apoptosis for weeks. Furthermore, we proposed a plausible model for chiral self-assembly peptides in 3-D culture. Our research may further stimulate others to design novel biological materials at single chiral amino acid level, and may broaden the applications of designer D-form self-assembling peptides in clinical and medical nanobiotechnology.

 Extended Potential-Gradient Architecture of a Phenylazomethine Dendrimer Imaoka, T.; Inoue, N.; Yamamoto, K. *Org. Lett.* **2013**, *15*, 1810-1813.
<u>Abstract:</u>



A dendritic nanoshell based on rigid phenylazomethine units was synthesized up to fifth generation around a zinc porphyrin core. Due to the finely organized sparse architecture, accessibility to the core can be discriminated by the size of the molecules and ionic species. By using this function, the lifetime of the photochemically produced radical ion pair can be extended over 200 times longer along with a good quantum yield.

 Tandem Ring-Closing Metathesis/Isomerization Reactions for the Total Synthesis of Violacein Petersen, M. T.; Nielsen, T. E. Org. Lett. 2013, 15, 1986-1989.
<u>Abstract:</u>



A series of 5-substituted 2-pyrrolidinones was synthesized through a one-pot ruthenium alkylidenecatalyzed tandem RCM/isomerization/nucleophilic addition sequence. The intermediates resulting from RCM/isomerization showed reactivity toward electrophiles in aldol condensation reactions which provided a new entry for the total synthesis of the antileukemic natural product violacein.

Tetrathiafulvalene–Oligo(*para*-phenyleneethynylene) Conjugates: Formation of Multiple Mixed-Valence Complexes upon Electrochemical Oxidation Lipnická, Š.; Bělohradský, M.; Kolivoška, V.; Pospíšil, L.; Hromadová, M.; Pohl, R.; Chocholoušová, J. V.; Vacek, J.; Fiedler, J.; Stará, I. G.; Starý, I. *Chem. Eur. J.* 2013, *19*, 6108–6121. Abstract:



Short monodisperse oligo- (*para*-phenyleneethynylene) (*p*OPE) units bearing laterally attached tetrathio-substituted tetrathiofulvalene (TTF) units have been synthesised from functionalised aromatic building blocks by using the Sonogashira cross-coupling methodology. The unusual redox properties of these TTF–*p*OPE conjugates were observed by employing electrochemical methods, such as cyclic voltammetry and exhaustive electrolysis. We found that formally one half of the TTF units in the *p*OPE monomer **1**, dimer **2**, and trimer **3** (with 2, 4, and 6 TTF units, respectively) are electrochemically silent during the first-step oxidation at 0.49 V. We propose the formation of persistent mixed-valence complexes from the TTF and TTF<sup>+.</sup> units present in an equal ratio. Such mixed-valence dyads (single or multiple in the partially oxidised **1–3**) exhibit an unusual stability towards oxidation until the potential of the second oxidation at 0.84 V is achieved. This finding suggests that below this potential the oxidation of the respective mix-valence complexes is extremely slow.

 Versatile Supramolecular Cross-Linker: A Rotaxane Cross-Linker That Directly Endows Vinyl Polymers with Movable Cross-Links Arai, T.; Jang, K.; Koyama, Y.; Asai, S.; Takata, T. *Chem. Eur. J.* 2013, *19*, 5917–5923. Abstract:



A supramolecular cross-linked cross-linker, capable of introducing rotaxane cross-links to vinyl polymers, has been developed for the rational synthesis of polyrotaxane networks. The experimental results reveal that the combination of an oligocyclodextrin (OCD) and a terminal bulky group-tethering macromonomer (TBM) forms a polymer-network structure having polymerizable moieties through supramolecular cross-linking. Radical polymerization of a variety of typical vinyl monomers in the presence of the vinylic supramolecular cross-linker (VSC) afforded the corresponding vinyl polymers cross-linked through the rotaxane cross-links (RCP) as transparent stable films in high yields under both photoinitiated and thermal polymerization conditions. A poly(*N*,*N*-dimethylacrylamide)-based hydrogel synthesized by using VSC, RCP<sub>DMAAm</sub>, displayed a unique mechanical property. The small-angle X-ray scattering (SAXS) results, indicating patterns characteristic of a polyrotaxane network, clearly suggested the presence and role of the rotaxane cross-links. The confirmation of the

introduction of rotaxane-cross-links into vinyl polymers strongly reveals the significant usefulness of VSC.

 Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene Butler, S. Z.; Hollen, S. M.; Cao, L.; Cui, Y.; Gupta, J. A.; Gutiérrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J.; Ismach, A. F.; Johnston-Halperin, E.; Kuno, M.; Plashnitsa, V. V.; Robinson, R. D.; Ruoff, R. S.; Salahuddin, S.; Shan, J.; Shi, L.; Spencer, M. G.; Terrones, M.; Windl, W.; Goldberger, J. E. ACS Nano 2013, 7, 2898-2926. <u>Abstract:</u>



Graphene's success has shown that it is possible to create stable, single and few-atom-thick layers of van der Waals materials, and also that these materials can exhibit fascinating and technologically useful properties. Here we review the state-of-the-art of 2D materials beyond graphene. Initially, we will outline the different chemical classes of 2D materials and discuss the various strategies to prepare single-layer, few-layer, and multilayer assembly materials in solution, on substrates, and on the wafer scale. Additionally, we present an experimental guide for identifying and characterizing single-layer-thick materials, as well as outlining emerging techniques that yield both local and global information. We describe the differences that occur in the electronic structure between the bulk and the single layer and discuss various methods of tuning their electronic properties by manipulating the surface. Finally, we highlight the properties and advantages of single-, few-, and many-layer 2D materials in field-effect transistors, spin- and valley-tronics, thermoelectrics, and topological insulators, among many other applications.

 Sampling a Biomarker of the Human Immunodeficiency Virus across a Synthetic Nanopore Niedzwiecki, D. J.; Iyer, R.; Borer, P. N.; Movileanu, L. ACS Nano 2013, 7, 3341-3350.
<u>Abstract:</u>



One primary goal in nanobiotechnology is designing new methodologies for molecular biomedical diagnosis at stages much earlier than currently possible and without use of expensive reagents and sophisticated equipment. In this work, we show the proof of principle for single-molecule detection

of the nucleocapsid protein 7 (NCp7), a protein biomarker of the HIV-1 virus, using synthetic nanopores and the resistive-pulse technique. The biosensing mechanism relied upon specific 17 interactions between NCp7 and aptamers of stem-loop 3 (SL3) in the packaging domain of the retroviral RNA genome. One critical step of this study was the choice of the optimal size of the nanopores for accurate, label-free determinations of the dissociation constant of the NCp7 protein– SL3 RNA aptamer complex. Therefore, we systematically investigated the NCp7 protein–SL3 RNA aptamer complex employing two categories of nanopores in a silicon nitride membrane: (i) small, whose internal diameter was smaller than 6 nm, and (ii) large, whose internal diameter was in the range of 7 to 15 nm. Here, we demonstrate that only the use of nanopores with an internal diameter that is smaller than or comparable with the largest cross-sectional size of the NCp7–SL3 aptamer complex enables accurate measurement of the dissociation constant between the two interacting partners. Notably, this determination can be accomplished without the need for prior nanopore functionalization. Moreover, using small solid-state nanopores, we demonstrate the ability to detect drug candidates that inhibit the binding interactions between NCp7 and SL3 RNA by using a test case of N-ethylmaleimide.