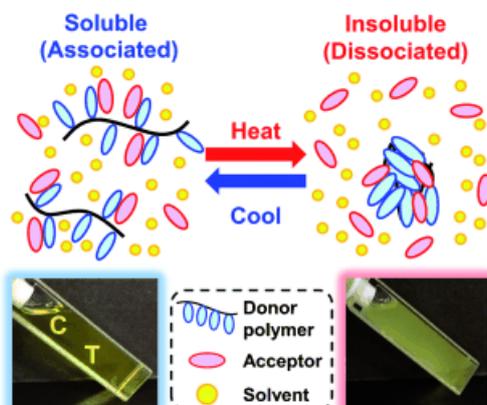


- Polymer Phase-Transition Behavior Driven by a Charge-Transfer Interaction  
Amemori, S.; Kokado, K.; Sada, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 4174–4178.

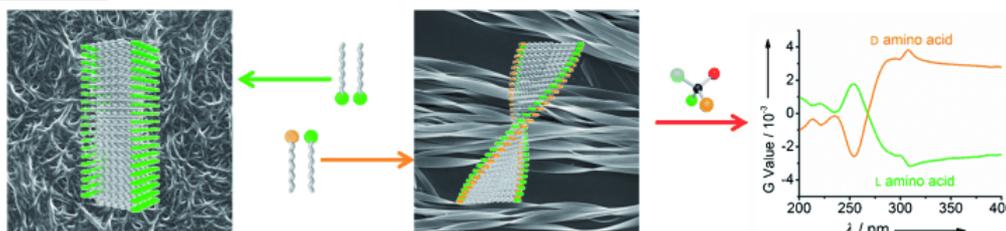
Abstract:



Cool down and get it together! The lower critical solution temperature (LCST) behavior of a polymer containing pyrene units was controlled by a charge-transfer (CT) interaction with an electron-accepting effector (see picture). The appearance of CT bands enabled quantitative evaluation of the thermodynamics of the association.

- Self-Assembly of Racemic Alanine Derivatives: Unexpected Chiral Twist and Enhanced Capacity for the Discrimination of Chiral Species  
Cao, H.; Zhu, X.; Liu, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 4122–4126.

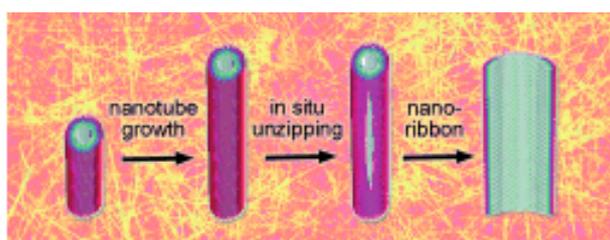
Abstract:



**Twisted ribbons** were formed by the self-assembly of racemic alanine derivatives (middle picture), whereas only flat nanostructures were obtained from the individual enantiomers (left). The twist was sensitive to a slight enantiomeric excess and showed remarkable macroscopic chirality. Moreover, it could discriminate various amino acid derivatives (right) and even enabled the determination of the *ee* value of a mixed system.

- High-Quality Boron Nitride Nanoribbons: Unzipping during Nanotube Synthesis  
Li, L.; Li, L. H.; Chen, X.; Dai, X. J.; Lamb, P. R.; Cheng, B.-M.; Lin, M.-Y.; Liu, X. *Angew. Chem. Int. Ed.* **2013**, *52*, 4212–4216.

Abstract:



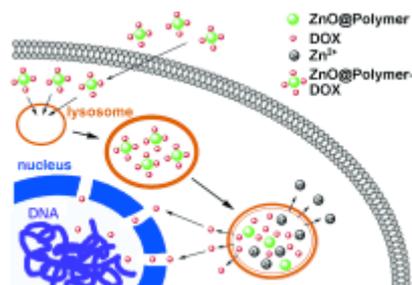
**Zipper examined:** High-quality boron nitride nanoribbons (BNNRs) can be produced directly during

nanotube synthesis without post-treatment. These BNNRs are typically several micrometers long and tens of nanometers wide. Near-edge X-ray absorption fine structure investigations indicated that the BNNRs are of high chemical purity and crystallinity.

- Biodegradable ZnO@polymer Core–Shell Nanocarriers: pH-Triggered Release of Doxorubicin In Vitro

Zhang, Z.-Y.; Xu, Y.-D.; Ma, Y.-Y.; Qiu, L.-L. ; Wang, Y.; Kong, J.-L. ; Xiong, H.-M. *Angew. Chem. Int. Ed.* **2013**, *52*, 4127-4131.

Abstract:

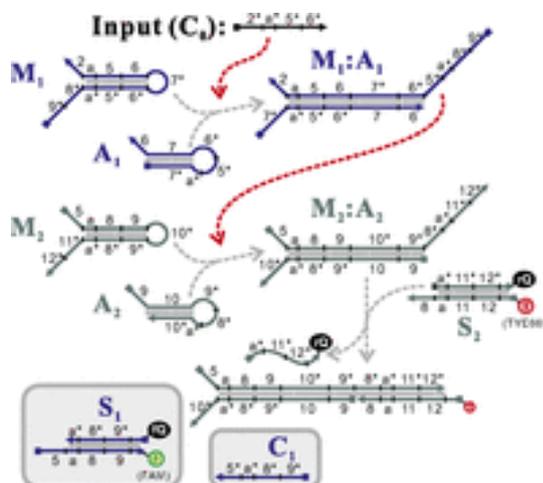


**Luminescent** ZnO@polymer core–shell nanoparticles were synthesized and loaded with doxorubicin (DOX) for the treatment of human brain cancer cells. Analyses by confocal laser scanning microscopy proved that the ZnO@polymer–DOX nanocomposites were decomposed at lysosomes to release DOX molecules, which penetrated into the nucleus and finally killed the cells (see picture).

- Stacking nonenzymatic circuits for high signal gain

Chen, X.; Briggs, N.; McLain, J. R.; Ellington, A. D. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 5386-5391.

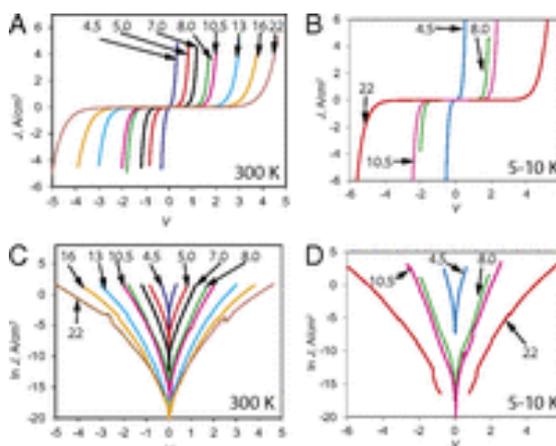
Abstract:



leakage. We successfully implemented a two-layer cascade that yielded 7,000-fold signal amplification and a two-stage, four-layer cascade that yielded upward of 600,000-fold signal amplification. Implementation of these unique methods and design principles should greatly empower molecular programming in general and DNA-based molecular diagnostics in particular.

- Activation-less charge transport across 4.5 to 22 nm in molecular electronic junctions  
Yan, H.; Bergren, A. J.; McCreery, R.; Della Rocca, M. L.; Martin, P.; Lafarge, P.; Lacroix, J. C. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 5326-5330.

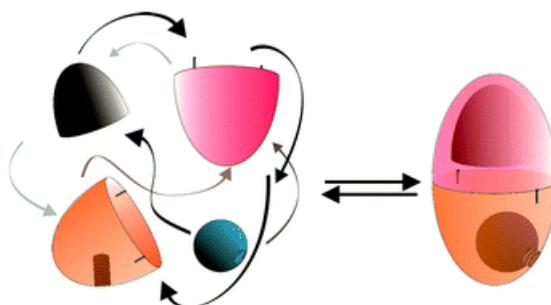
Abstract:



In this work, we bridge the gap between short-range tunneling in molecular junctions and activated hopping in bulk organic films, and greatly extend the distance range of charge transport in molecular electronic devices. Three distinct transport mechanisms were observed for 4.5–22-nm-thick oligo(thiophene) layers between carbon contacts, with tunneling operative when  $d < 8$  nm, activated hopping when  $d > 16$  nm for high temperatures and low bias, and a third mechanism consistent with field-induced ionization of highest occupied molecular orbitals or interface states to generate charge carriers when  $d = 8$ –22 nm. Transport in the 8–22-nm range is weakly temperature dependent, with a field-dependent activation barrier that becomes negligible at moderate bias. We thus report here a unique, activationless transport mechanism, operative over 8–22-nm distances without involving hopping, which severely limits carrier mobility and device lifetime in organic semiconductors. Charge transport in molecular electronic junctions can thus be effective for transport distances significantly greater than the 1–5 nm associated with quantum-mechanical tunneling.

- Hydrogen bonded supramolecular capsules with functionalized interiors: the controlled orientation of included guests  
Adriaenssens, L.; Ballester, P. *Chem. Soc. Rev.* **2013**, *42*, 3261-3277.

Abstract:

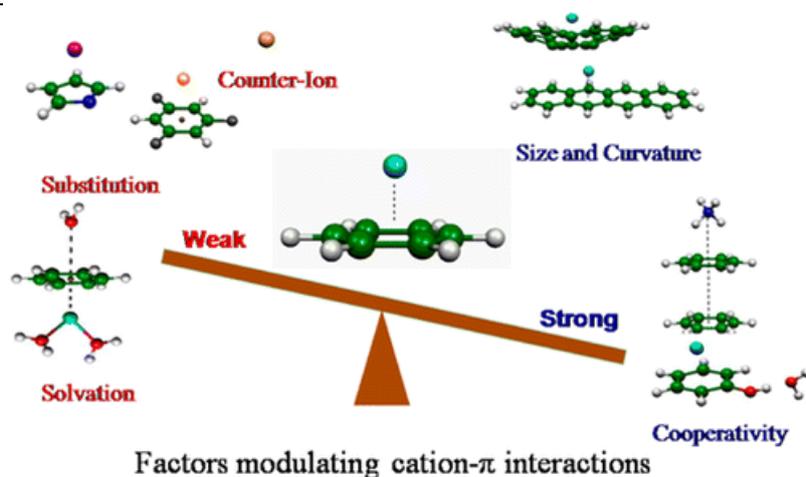


This tutorial review aims to present and describe selected examples of still quite rare *endo-*

functionalized supramolecular capsules. Only capsules assembled through the use of neutral or polar hydrogen bonding interactions are covered. The ability of these capsules to orient and control the position of the encapsulated guest molecules represents their stand-out feature. Thus, the way in which guests interact with the functionalized interior of the capsules is discussed in detail. Several of the described capsular assemblies display chiral architectures. The manner in which chirality is manifested in these assemblies is far from trivial. For this reason, we also offer explanations of the chiral features expressed by the relevant capsules and their encapsulation complexes.

- Cation- $\pi$  Interaction: Its Role and Relevance in Chemistry, Biology, and Material Science Mahadevi, A. S.; Sastry, G. N. *Chem. Rev.* **2013**, *113*, 2100–2138.

Abstract:



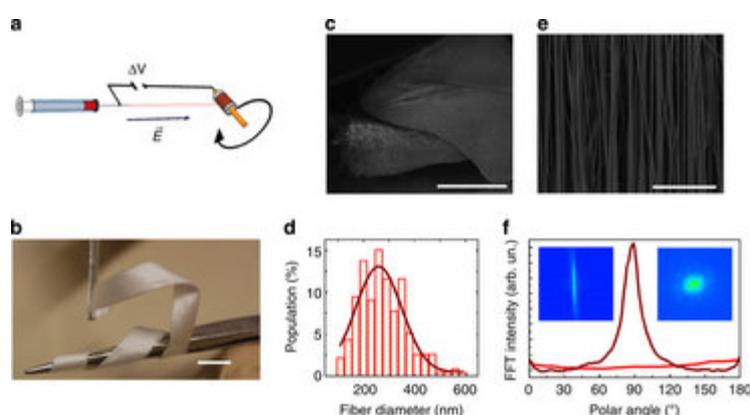
Noncovalent interactions are essential for the existence of solid and liquid phases. Traditionally touted as weak forces, quantification of these interactions, which govern the molecular aggregation and determine the supramolecular assembly, is of fundamental interest. Hydrogen bonding has been extremely well studied and recognized as the most important of all noncovalent interactions. In recent years a great deal of attention is given to understand various kinds of weak interactions such as hydrophobic interaction, dispersion interaction, halogen bonding, anion- $\pi$  interaction, salt bridge interaction, intercalation and CH- $\pi$ , NH- $\pi$ , OH- $\pi$ , and SH- $\pi$  interactions, etc. Several studies are directed toward understanding the nature, type, extent, and relevance of hydrogen bonding in chemical and biological systems. Apart from hydrogen bond, two major interactions, namely,  $\pi$ - $\pi$  stacking and cation- $\pi$  interaction, have emerged as the forces of outstanding importance in controlling the structure and function of macromolecules in recent years. In general, stacking interactions are weaker compared to hydrogen bonding while cation- $\pi$  interactions tend to be stronger. Cation- $\pi$  interactions are ubiquitous and are of prime importance in several fields of contemporary interest, such as chemistry, material science, biology, and allied areas. Although these interactions were noticed about three decades ago, their significance and importance has been firmly established in recent years. Cation- $\pi$  interaction is essentially of electrostatic origin because a positively charged cation interacts with negatively charged electron cloud of  $\pi$  systems, and thus, it is arguably the strongest among the noncovalent interactions. Such strong interactions, obviously, are expected to have a profound influence in controlling the neighboring structural environment. Under certain circumstances, cation- $\pi$  interactions may also be relatively weak depending on the nature of cation, whether it is coordinately saturated or not and also on the nature of the  $\pi$  acceptor and hence the range that is spanned by them is quite vast. In the current era of nanotechnology, understanding

the nature, range and relevance of cation- $\pi$  interaction is of outstanding importance in designing molecules and materials. In this Review, we present the relevance and role of cation- $\pi$  interactions in chemistry, biology, material science, and nanosystems. Particular attention is paid to understand the factors responsible in modulating the cation- $\pi$  interaction along with their structural and functional significance. The review summarizes the significant experimental, computational, and database studies involving cation- $\pi$  interactions because an effective interplay among these fields is warranted for obtaining deeper insights.

- High performance piezoelectric devices based on aligned arrays of nanofibers of poly(vinylidene fluoride-co-trifluoroethylene)

Persano, L.; Dagdeviren, C.; Su, Y.; Zhang, Y.; Girardo, S.; Pisignano, D.; Huang, Y.; Rogers, J. A. *Nature Commun.* **2013**, *4*, 1633.

Abstract:

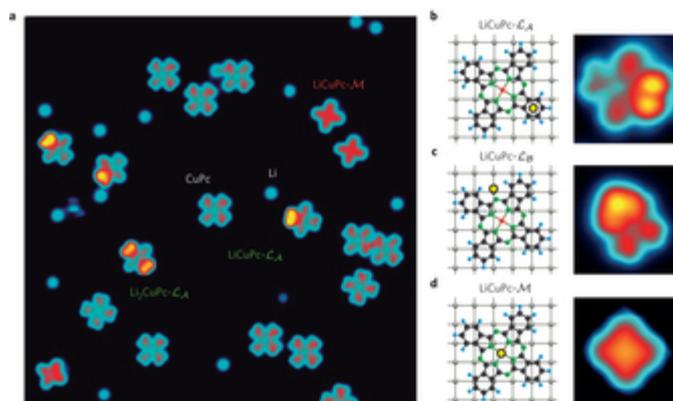


Multifunctional capability, flexible design, rugged lightweight construction and self-powered operation are desired attributes for electronics that directly interface with the human body or with advanced robotic systems. For these applications, piezoelectric materials, in forms that offer the ability to bend and stretch, are attractive for pressure/force sensors and mechanical energy harvesters. Here, we introduce a large area, flexible piezoelectric material that consists of sheets of electrospun fibres of the polymer poly[(vinylidene fluoride-co-trifluoroethylene)]. The flow and mechanical conditions associated with the spinning process yield free-standing, three-dimensional architectures of aligned arrangements of such fibres, in which the polymer chains adopt strongly preferential orientations. The resulting material offers exceptional piezoelectric characteristics, to enable ultra-high sensitivity for measuring pressure, even at exceptionally small values (0.1 Pa). Quantitative analysis provides detailed insights into the pressure sensing mechanisms, and establishes engineering design rules. Potential applications range from self-powered micro-mechanical elements, to self-balancing robots and sensitive impact detectors.

- Site- and orbital-dependent charge donation and spin manipulation in electron-doped metal phthalocyanines

Krull, C.; Robles, R.; Mugarza, A.; Gambardella, P. *Nature Mater.* **2013**, *12*, 337–343.

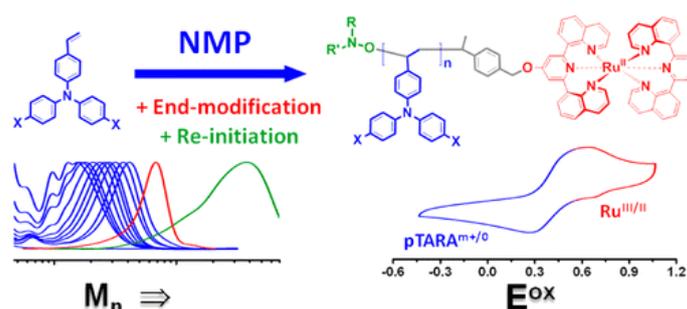
Abstract:



Chemical doping offers promise as a means of tailoring the electrical characteristics of organic molecular compounds. However, unlike for inorganic semiconductors used in electronics applications, controlling the influence of dopants in molecular complexes is complicated by the presence of multiple doping sites, electron acceptor levels, and intramolecular correlation effects. Here we use scanning tunnelling microscopy to analyse the position of individual Li dopants within Cu- and Ni-phthalocyanine molecules in contact with a metal substrate, and probe the charge transfer process with unprecedented spatial resolution. We show that individual phthalocyanine molecules can host at least three distinct stable doping sites and up to six dopant atoms, and that the ligand and metal orbitals can be selectively charged by modifying the configuration of the Li complexes. Li manipulation reveals that charge transfer is determined solely by dopants embedded in the molecules, whereas the magnitude of the conductance gap is sensitive to the molecule–dopant separation. As a result of the strong spin–charge correlation in confined molecular orbitals, alkali atoms provide an effective way for tuning the molecular spin without resorting to magnetic dopants.

- Nitroxide-Mediated Polymerization of Styrenic Triaryl Amines and Chain-End Functionalization with a Ruthenium Complex: Toward Tailored Photoredox-Active Architectures  
Schroot, R.; Friebe, C.; Altuntas, E.; Crotty, S.; Jäger, M.; Schubert, U. S. *Macromolecules* **2013**, *46*, 2039-2048.

Abstract:

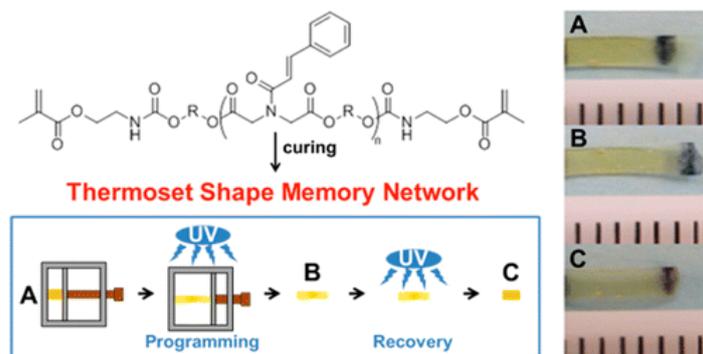


The preparation of redox-active polymers and the chain-end functionalization with one ruthenium complex was investigated in detail. A series of substituted monomers, i.e., styrenic triaryl amines bearing methyl, fluoro, or methoxy substituents, were prepared by a one-pot Hartwig–Buchwald coupling. The nitroxide-mediated polymerization (NMP) was studied by variation of the functional initiators, the monomer-to-initiator ratios, and the solvent. The kinetic analysis of the prototypical methyl-substituted triaryl amine shows the controlled polymerization up to 75% conversion, but a considerable decrease of the polymerization rate was observed during the course of the reaction. Both chain-end functionalities of the purified oligomers were subsequently utilized, i.e., the nitroxide to serve as a macroinitiator for an additional NMP step and the chloromethyl group to introduce one

ruthenium complex at the chain terminus. The products were analyzed in detail by size-exclusion chromatography, NMR spectroscopy, and mass spectrometry. The optical and electrochemical properties of the prepared poly(triarylamine)s show the application potential as charge transport materials in conjunction with the photoactive ruthenium complex.

- Photoresponsive Polyesters for Tailorable Shape Memory Biomaterials  
Rochette, J. M.; Ashby, V. S. *Macromolecules* **2013**, *46*, 2134-2140.

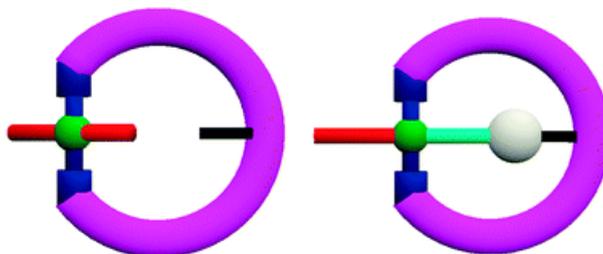
Abstract:



The synthesis of a library of poly(ester urethane)s (PEUs) containing pendant photoresponsive moieties afforded through the incorporation of one of two novel bifunctional monomers resulted in degradable materials with a range of tunable thermal and mechanical properties. Utilizing light irradiation, macroscopic temporary shapes were fixed by increasing the cross-link density of a thermoset network via photoinduced reversible [2 + 2] cycloaddition of cinnamamide or cinnamate pendant groups under UV light ( $\lambda = 302$  nm). Further irradiation with UV light ( $\lambda = 254$  nm) led to the cleaving of the temporary cross-links and recovery of the original shape. Examination of these materials under physiological conditions displayed tunable degradation with rates faster than PCL-based materials, and initial biocompatibility studies exhibited negligible cytotoxicity for HeLa cells based on results of ATP assay. The ability to tune thermal properties also allowed specific polymer compositions to boast transition temperatures within a range of applicable temperature for thermal shape memory.

- A platinum based organometallic turnstile  
Zigon, N.; Guenet, A.; Graf, E.; Hosseini, M. W. *Chem. Commun.* **2013**, *49*, 3637-3639.

Abstract:

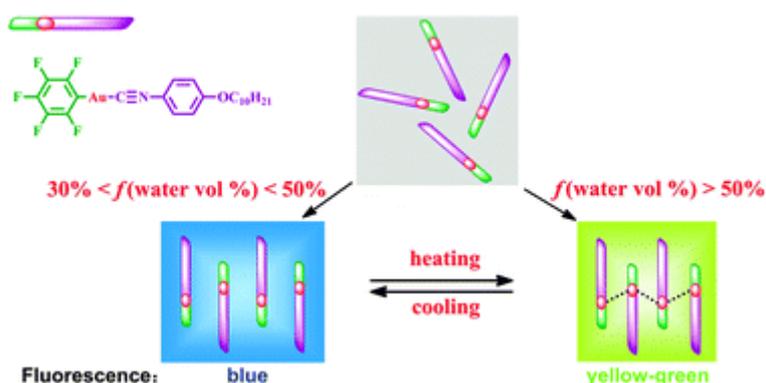


The synthesis of an organometallic turnstile based on a Pt(II) centre as a hinge was achieved. Its dynamic behaviour in solution was investigated using 1D and 2D NMR techniques. Using Ag(I) cation as an effector, the switching between its open and closed states in solution was demonstrated.

- Aggregation-induced emission (AIE) behavior and thermochromic luminescence properties of a new gold(I) complex

Liang, J.; Chen, Z.; Yin, J.; Yu, G.-A.; Liu, S. H. *Chem. Commun.* **2013**, 49, 3567-3569.

Abstract:

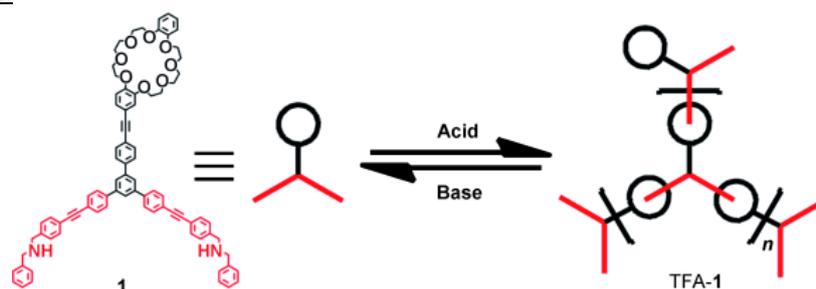


A new gold complex that shows the AIE effect as well as the thermochromic fluorescence switch is reported. This interesting phenomenon is attributed to changes in the intermolecular AuAu interactions and the formation of nano-aggregates.

- pH-Controlled Reversible Formation of a Supramolecular Hyperbranched Polymer Showing Fluorescence Switching

Yu, B.; Wang, B.; Guo, S.; Zhang, Q.; Zheng, X.; Lei, H.; Liu, W.; Bu, W.; Zhang, Y.; Chen, X. *Chem. Eur. J.* **2013**, 19, 4922–4930.

Abstract:



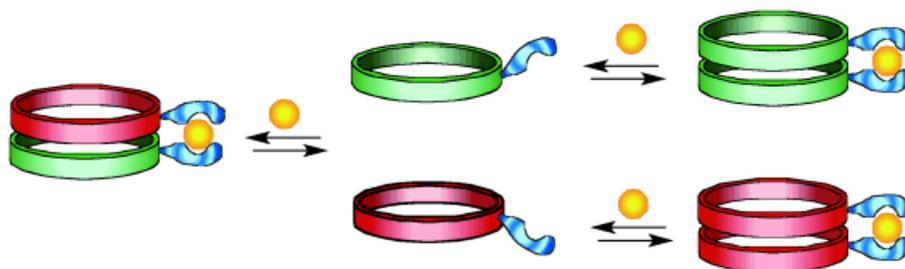
**Branching out:** A supramolecular hyperbranched polymer, TFA-1, has been reversibly fabricated by successively adding acid and base to a conjugated AB<sub>2</sub> monomer (**1**) in CH<sub>2</sub>Cl<sub>2</sub> (see scheme). The driving force behind its assembly is based on acid–base-controllable host–guest recognition between the dibenzo[24]crown-8 moiety and dialkylammonium ion centres. This reversible process is associated with the establishment of  $\pi$ – $\pi$  stacking interactions between the conjugated cores in solution, which affects the observed fluorescence intensity.

A  $\pi$ -conjugated AB<sub>2</sub> monomer **1** with a dibenzo[24]crown-8 (DB24C8) ring and two secondary amine centres has been synthesised. Treatment of a solution of **1** in dichloromethane with trifluoroacetic acid (TFA) leads to protonation of the amine groups, and then the DB24C8 rings are threaded by the dialkylammonium ion centres of other monomer molecules, leading to the formation of a supramolecular hyperbranched polymer, TFA-1. Rather strong  $\pi$ – $\pi$  stacking interactions between the conjugated cores are evident in this polymer. The supramolecular hyperbranched polymer (SHP) can be completely depolymerised by adding a slight excess of *N*-*tert*-butyl-*N*',*N*',*N*'',*N*'',*N*'',*N*'''-hexamethylphosphorimidic triamide, tetrabutylammonium fluoride, or tetrabutylammonium acetate. The acid–base-controlled process induces a reversible change in the fluorescence intensities of the solutions due to the controllable presence of the  $\pi$ – $\pi$  stacking interactions between the conjugated cores. This dynamic behaviour is significant with respect to “smart” supramolecular polymer materials.

- Design of Stable  $\beta$ -Sheet-Based Cyclic Peptide Assemblies Assisted by Metal Coordination: Selective Homo- and Heterodimer Formation

Panciera, M.; Amorín, M.; Castedo, L.; Granja, J. R. *Chem. Eur. J.* **2013**, *19*, 4826–4834.

Abstract:

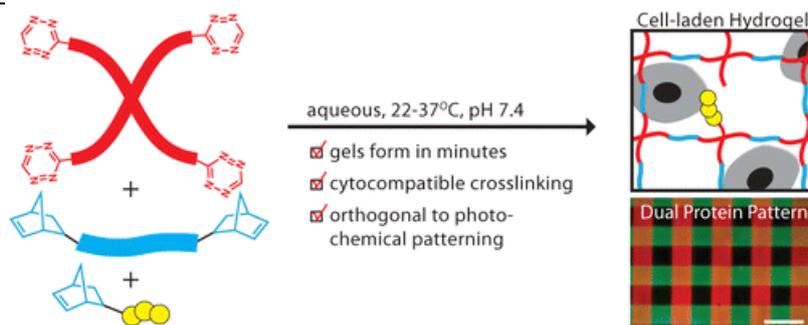


**Metal tweezers:** The self-assembling properties of  $\alpha,\gamma$ -cyclic peptides are reinforced by metal coordination to precisely construct homo- and heterodimeric complexes. The metal coordination is able to shift the equilibrium from several nonequivalent dimers to one single ensemble (see scheme). Metal-directed supramolecular construction represents one of the most powerful tools to prepare a large variety of structures and functions. The ability of metals to organize different numbers and types of ligands with a variety of geometries (linear, trigonal, octahedral, etc.) expands the supramolecular synthetic architecture. We describe here the precise construction of homo- and heterodimeric cyclic peptide entities through coordination of a metal (Pd, Au) and to  $\beta$ -sheet-type hydrogen-bonding interactions. The selective coordination properties of the appropriate metal allow control over the cross-strand interaction between the two-peptide strands.

- Synthetically Tractable Click Hydrogels for Three-Dimensional Cell Culture Formed Using Tetrazine–Norbornene Chemistry

Alge, D. L.; Azagarsamy, M. A.; Donohue, D. F.; Anseth, K. S. *Biomacromolecules* **2013**, *14*, 949–953.

Abstract:

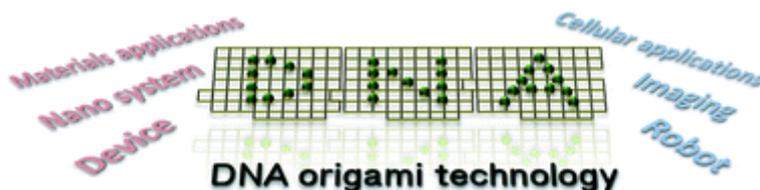


The implementation of bio-orthogonal click chemistries is a topic of growing importance in the field of biomaterials, as it is enabling the development of increasingly complex hydrogel materials capable of providing dynamic, cell-instructive microenvironments. Here, we introduce the tetrazine–norbornene inverse electron demand Diels–Alder reaction as a new cross-linking chemistry for the formation of cell laden hydrogels. The fast reaction rate and irreversible nature of this click reaction allowed for hydrogel formation within minutes when a multifunctional PEG-tetrazine macromer was reacted with a dinorbornene peptide. In addition, the cytocompatibility of the polymerization led to high postencapsulation viability of human mesenchymal stem cells, and the specificity of the tetrazine–norbornene reaction was exploited for sequential modification of the network via thiol–

ene photochemistry. These advantages, combined with the synthetic accessibility of the tetrazine molecule compared to other bio-orthogonal click reagents, make this cross-linking chemistry an interesting and powerful new tool for the development of cell-instructive hydrogels for tissue engineering applications.

- DNA origami technology for biomaterials applications  
Endo, M.; Yang, Y.; Sugiyama, H. *Biomater. Sci.* **2013**, *1*, 347-360.

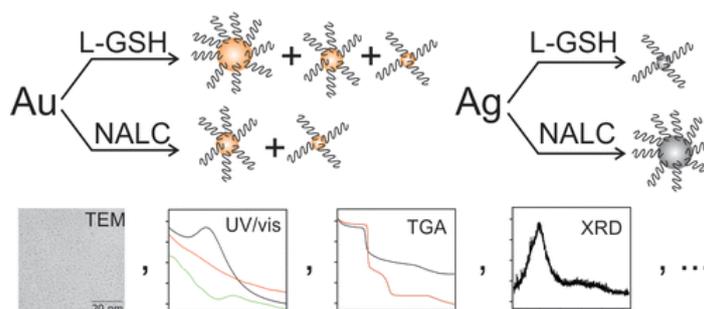
Abstract:



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.

- Chiral Gold and Silver Nanoclusters: Preparation, Size Selection, and Chiroptical Properties  
Farrag, M.; Tschurl, M.; Heiz, U. *Chem. Mater.* **2013**, *25*, 862-870.

Abstract:

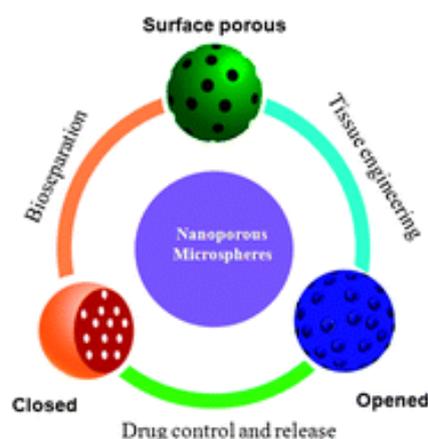


In this work we studied different properties of gold and silver nanoclusters (AuNCs and AgNCs) protected by the chiral ligands l-glutathione (L-GSH), and *N*-acetyl-l-cysteine (NALC), and we present a thorough characterization of the synthesized clusters. The synthesis was performed by reduction of the corresponding metal salt with  $\text{NaBH}_4$ . Fractions of gold nanoclusters with different sizes were isolated by methanol-induced precipitation. The ellipticity of the clusters was obtained by circular dichroism (CD) spectroscopy, showing that the chirality of the ligands is transferred to the metal core either in its structure or at least in its electronic states via perturbation of the electronic field of the ligands. The optical properties of gold and silver nanoclusters in water were studied by UV-vis spectroscopy. The absorption signal of the clusters shows characteristic bands, which can be assigned to plasmonic transitions of the metal core. In addition, UV-vis spectroscopy has served as a tool for studying the stability of these clusters in air. In general, gold nanoclusters are highly stable in air, and

it was found that the stability of  $Au_n(NALC)_m$  clusters even exceeds that of  $Au_n(SG)_m$  clusters. In contrast to gold clusters, silver nanoclusters very often tend to decompose upon exposure to air. We found, however, that  $Ag_n(NALC)_m$  are surprisingly stable at atmospheric pressures. The average molecular formula of the nanoclusters was determined by thermogravimetric analysis (TGA). The particle sizes of AuNCs and AgNCs were assessed by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) analysis. For studying the fluorescent properties of the metal nanoparticles, photoluminescence spectroscopy (PL) was performed. In summary, we succeeded to synthesize ligand-protected silver clusters ( $Ag_n(NALC)_m$ ) with very high stability and rather narrow size distribution; furthermore, we could show the controlled precipitation to be applicable to other systems, such as that  $Au_n(NALC)_m$ , yielding two fraction of very narrow size distribution.

- Nanoporous microspheres: from controllable synthesis to healthcare applications  
Fan, J.-B.; Huang, C.; Jiang, L.; Wang, S. *J. Mater. Chem. B* **2013**, *1*, 2222-2235.

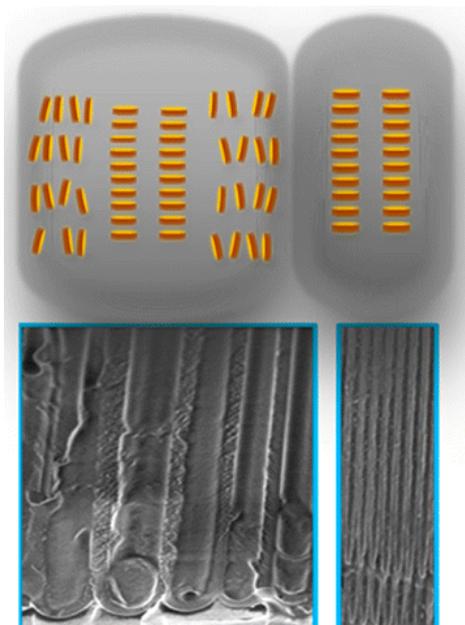
Abstract:



Multiscale nanoporous microspheres have attracted great research interest in multiple fields, such as separation, catalysis, sensors, energy storage, tissues engineering and drug release, due to their excellent permeability, high surface area, low density and stable mechanical properties. In this review, well-defined nanoporous microspheres ranging from inorganic to organic nanoporous microspheres are presented and categorized. First, we classify nanoporous microspheres into three main structural categories that include an “opened” nanoporous microsphere, a “closed” nanoporous microsphere and surface nanoporous microspheres. The corresponding approaches to fabricating these nanoporous microspheres are further presented, which mainly include hydrothermal/solvothermal synthesis, thermal decomposition, suspension polymerization, dispersion polymerization, precipitation polymerization, emulsion polymerization, multiple emulsion–solvent evaporation, template and microfluidic methods. In addition, our discussions focus on the healthcare applications of nanoporous microspheres, such as bioseparation, drug control and release and tissue engineering. This review will be expected to provide a comprehensive guide to the design and synthesis of functional nanoporous microspheres that closely relate to healthcare applications.

- Arrays of Aligned Supramolecular Wires by Macroscopic Orientation of Columnar Discotic Mesophases  
Duran, H.; Hartmann-Azanza, B.; Steinhart, M.; Gehrig, D.; Laquai, F.; Feng, X.; Müllen, K.; Butt, H.-J.; Floudas, G. *ACS Nano* **2012**, *6*, 9359-9365.

Abstract:

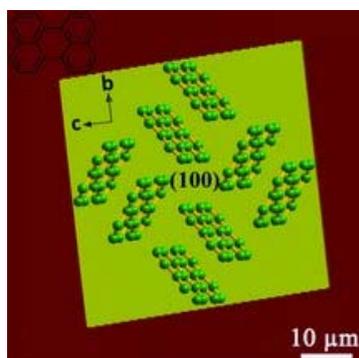


Structure formation, phase behavior, and dynamics of mono-bromo hexa-peri-hexabenzocoronene (HBC-Br) are strongly affected by the confinement of cylindrical nanopores with rigid walls. Using self-ordered nanoporous anodic aluminum oxide (AAO)-containing arrays of aligned nanopores with narrow size distribution as a confining matrix, pronounced alignment of the HBC-Br columns along the nanopore axes was found to be independent of the pore diameter. Hence, arrays of one-dimensional supramolecular HBC-Br wires with the columns uniformly oriented along the wire axes on a macroscopic scale were obtained, unlike with discotics bearing smaller cores. The formation of the crystalline herringbone structure is shifted to lower temperatures in nanopores with diameters of a few hundred nanometers, whereas the formation of this low-temperature phase is completely suppressed when the pore diameter is below 20 lattice parameters. Moreover, the cylindrical confinement affects the disk axial dynamics as well as the distribution of relaxation times.

- Atomically Flat, Large-Sized, Two-Dimensional Organic Nanocrystals

Jiang, H.; Zhang, K. K.; Ye, J.; Wei, F.; Hu, P.; Guo, J.; Liang, C.; Chen, X.; Zhao, X.; McNeil, L. E.; Hu, W.; Kloc, C. *Small* **2013**, *9*, 990–995.

Abstract:

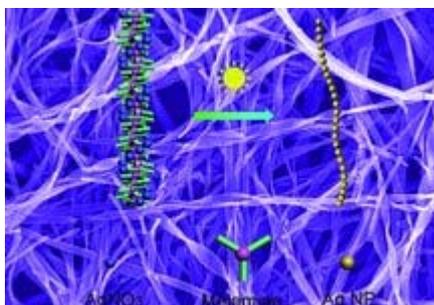


Large-sized, 2D single crystals of perylene are grown by both solution-cast and physical vapor transport methods. The crystals have an atomically flat parallelogram morphology and the aspect ratios of the lateral extension compared to the thickness are up to 103. The atomically flat feature leads to good interface contact, making a single-crystal field-effect transistor with higher mobility. The mobility of atomically flat crystals can be 10<sup>3</sup>–10<sup>4</sup> times higher than rough crystals.

- Responsive Helical Self-Assembly of  $\text{AgNO}_3$  and Melamine Through Asymmetric Coordination for Ag Nanochain Synthesis

Fei, J.; Gao, L.; Zhao, J.; Du, C.; Li, J. *Small* **2013**, *9*, 1021–1024.

Abstract:

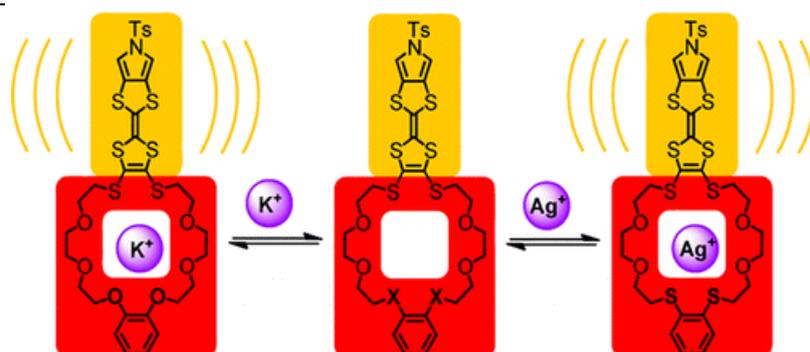


Responsive nanohelices can be self-assembled via asymmetric coordination bonding between  $\text{AgNO}_3$  and melamine. Silver nanochains composed of nanoparticles can be synthesized simply by photo-reduction of the above complex.

- Selective Redox-Active Molecular Receptors for  $\text{K}^+$  and  $\text{Ag}^+$

Larsen, K. R.; Johnsen, C.; Hammerich, O.; Jeppesen, J. O. *Org. Lett.* **2013**, *15*, 1452–1455.

Abstract:

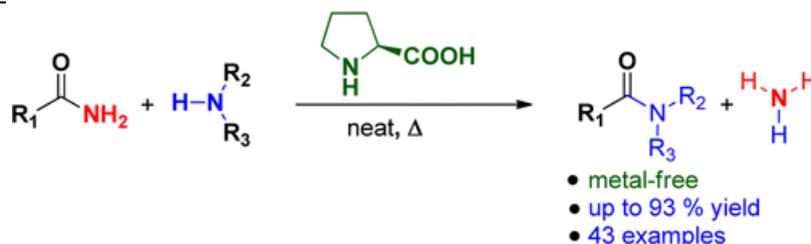


Two new tetrathiafulvalene based receptors in which the favorable redox properties of the tetrathiafulvalene unit are coupled to either a benzocrown ( $X = \text{O}$ ) or a dithiabenzocrown ( $X = \text{S}$ ) ether binding site were designed and synthesized as receptors for  $\text{K}^+$  and  $\text{Ag}^+$ . The receptors display good ( $\text{K}^+$ ,  $X = \text{O}$ ) to strong ( $\text{Ag}^+$ ,  $X = \text{S}$ ) affinity toward the cation and a high discrimination against other metal cations.

- L-Proline: An Efficient Catalyst for Transamidation of Carboxamides with Amines

Rao, S. N.; Mohan, D. C.; Adimurthy, S. *Org. Lett.* **2013**, *15*, 1496–1499.

Abstract:



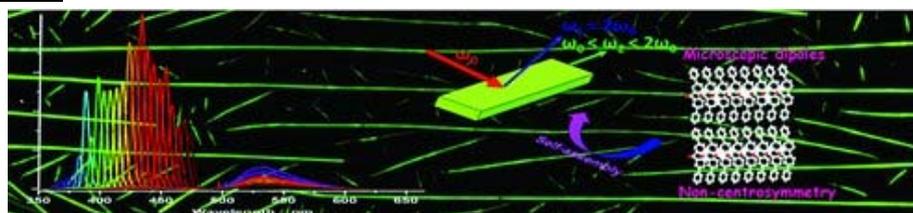
In the presence of a catalytic amount of L-proline (10 mol %), transamidations of carboxamides with amines were achieved under solvent-free conditions. The transamidation process is compatible with

a wide range of amines.

- Self-Assembled Organic Microfibers for Nonlinear Optics

Xu, J.; Semin, S.; Niedzialek, D.; Kouwer, P. H. J.; Fron, E.; Coutino, E.; Savoini, M.; Li, Y.; Hofkens, J.; Uji-I, H.; Beljonne, D.; Rasing, T.; Rowan, A. E. *Adv. Mater.* **2013**, *25*, 2084–2089.

Abstract:

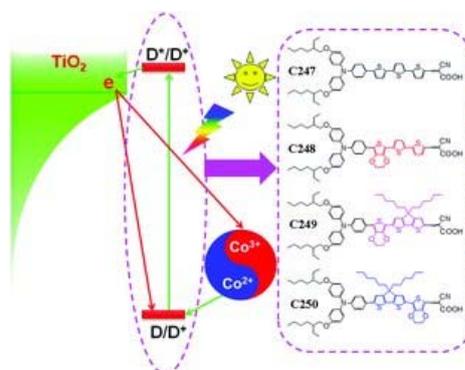


While highly desired in integrated optical circuits, multiresponsive and tunable nonlinear optical (NLO) active 1D (sub)wavelength scale superstructures from organic materials are rarely reported due to the strong tendency of organic molecules to self-assembly in centrosymmetric modes. Here a solution-processed assembly approach is reported to generate non-centrosymmetric single-crystalline organic microfibers with a cumulative dipole moment for anisotropic combined second- and third-order NLO.

- Engineering of Push-Pull Thiophene Dyes to Enhance Light Absorption and Modulate Charge Recombination in Mesoscopic Solar Cells

Cai, N.; Wang, Y.; Xu, M.; Fan, Y.; Li, R.; Zhang, M.; Wang, P. *Adv. Funct. Mater.* **2013**, *23*, 1846–1854.

Abstract:

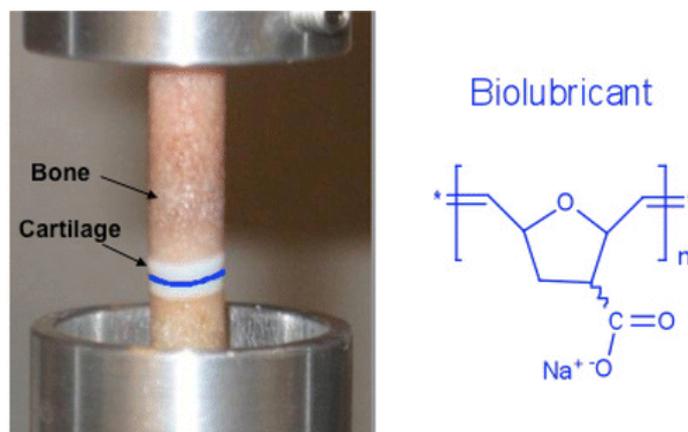


The elaborate selection of diverse  $\pi$ -conjugated segments which bridge the electron donors and acceptors in organic push-pull dyes can not only tune the molecular energy-levels but also impact the interfacial energetics and kinetics of dye-sensitized solar cells (DSCs). In this paper, a series of triphenylamine-cyanoacrylic acid photosensitizers is reported with TT, EDOT-BT, EDOT-CPDT, and CPDT-EDOT (herein TT, EDOT, BT, and CPDT denote terthiophene, ethylenedioxythiophene, bithiophene, and cyclopentadithiophene, respectively) as the  $\pi$ -linkers, and the dye-structure correlated photocurrent and photovoltage features of DSCs based on a cobalt electrolyte are scrutinized via analyzing light absorption and multichannel charge transfer kinetics. Both stepwise incorporation of more electron-rich blocks and rational modulation of connection order of dissimilar segments can result in a negative movement of ground-state redox potential and a red-shift of the absorption peak. While these styles of reducing energy-gap do not exert too much influence on the electron injection from photoexcited dye molecules to titania, the dyestuff employing the EDOT-BT linker presents a faster interfacial charge recombination and a slower dye regeneration, accounting

for its inferior cell efficiency of 5.3% compared to that of 9.4% at the AM1.5G conditions achieved by the CPDT-EDOT dye.

- A Large-Molecular-Weight Polyanion, Synthesized via Ring-Opening Metathesis Polymerization, as a Lubricant for Human Articular Cartilage  
Wathier, M.; Lakin, B. A.; Bansal, P. N.; Stoddart, S. S.; Snyder, B. D.; Grinstaff, M.W. *J. Am. Chem. Soc.* **2013**, *135*, 4930–4933.

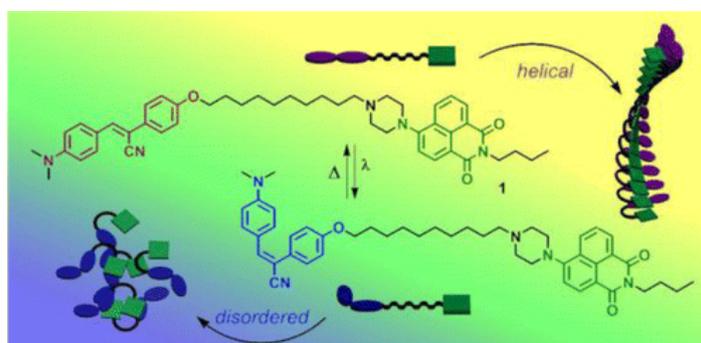
Abstract:



A large-molecular-weight polyanion is found to possess lubricating properties for cartilage. The polyanion, sodium poly(7-oxanorbornene-2-carboxylate), is synthesized by ring-opening metathesis polymerization of methyl 5-oxanorbornene-2-carboxylate. When dissolved in aqueous solution and applied to the surface of human cartilage it reduces the friction at the interface and acts as a lubricant. Its performance is similar to that of synovial fluid and superior to those of saline and Synvisc in an ex vivo human cartilage plug-on-plug model. The polymer is also not readily degraded by hyaluronidase or cytotoxic to human chondrocytes in vitro. As such, this polymer is a new type of viscosupplement, and the results provide insight into the design requirements for synthesizing highly efficacious synthetic biolubricants.

- Unimolecular Photoconversion of Multicolor Luminescence on Hierarchical Self-Assemblies  
Zhu, L.; Li, X.; Zhang, Q.; Ma, X.; Li, M.; Zhang, H.; Luo, Z.; Ågren, H.; Zhao, Y. *J. Am. Chem. Soc.* **2013**, *135*, 5175–5182.

Abstract:



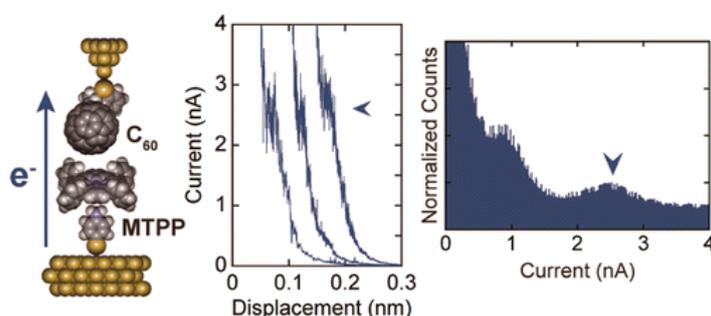
Facile tuning of photophysical properties is highly desirable for boosting the performance and versatility of photoluminescent materials. In an attempt to overcome the challenge of achieving the photoswitching of multicolor luminescence on unimolecular platforms, we here report a novel hierarchical self-assembly of a cyanostilbene–naphthalimide dyad as the realization of phototunable

luminescence at the unimolecular level. The work takes advantage of the photoisomerization of the cyanostilbene moiety from the Z form to its E form, which causes a morphological disorder in the molecular self-assembly and gives rise to a dual fluorescent characteristic accompanied by a progressive luminescent color conversion from yellow to green and finally to blue. Such systems with convertible multicolor luminescence might exhibit application potentials for unimolecular selective imaging and labeling, as exemplified by the cell imaging studies presented in this work.

- Quantitative Exploration of Electron Transfer in a Single Noncovalent Supramolecular Assembly

Bui, P. T.; Nishino, T.; Yamamoto, Y.; Shiigi, H. *J. Am. Chem. Soc.* **2013**, *135*, 5238–5241.

Abstract:

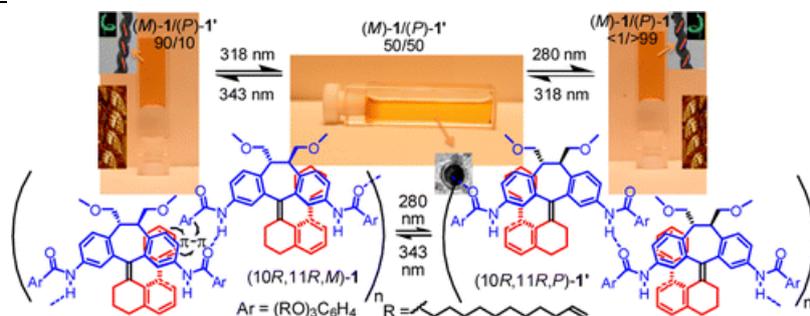


Electron transfer through a noncovalent interaction bears essential relevance to the functions of bottom-up supramolecular assembly. However, rather little knowledge regarding such phenomena at the single-molecule level is currently available. Herein we report the direct quantification of electron-transfer processes for a single noncovalently linked porphyrin–fullerene dyad. Facilitated electron transfer via a charge-transfer interaction in-between was successfully measured by utilizing a fullerene molecular tip. The rectification property of the supramolecular assembly was determined and quantitatively assessed. The present study opens up a way to explore quantitatively the rich electronic properties of supramolecules at the single-molecule level.

- Complementary Helicity Interchange of Optically Switchable Supramolecular-Enantiomeric Helicenes with (-)-Gel-Sol-(+)-Gel Transition Ternary Logic

Chen, C.-T.; Chen, C.-H.; Ong, T.-G. *J. Am. Chem. Soc.* **2013**, *135*, 5294–5297.

Abstract:

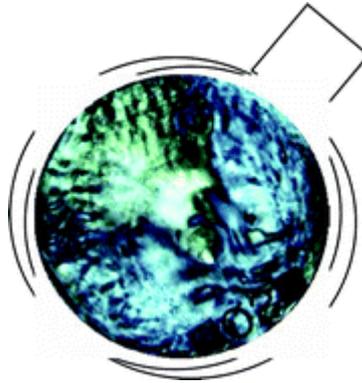


A gallamide-containing pseudoenantiomeric helicene pair bearing a (10*R*,11*R*)-dimethoxymethyldibenzosuberane core can self-assemble by intermolecular amide H-bonding and  $\pi$ - $\pi$  stacking into bundled helical fibers with helical tunnels of complementary helicity in  $\text{CH}_2\text{Cl}_2$ . The helicenes undergo excellent complementary photoswitchings of ternary logic at 280, 318, and 343 nm through (-)-gel-sol-(+)-gel interconversion.

- Structural arrest and texture dynamics in suspensions of charged colloidal rods

Kang, K.; Dhont, J. K. G. *Soft Matter* **2013**, *9*, 4401-4411.

Abstract:

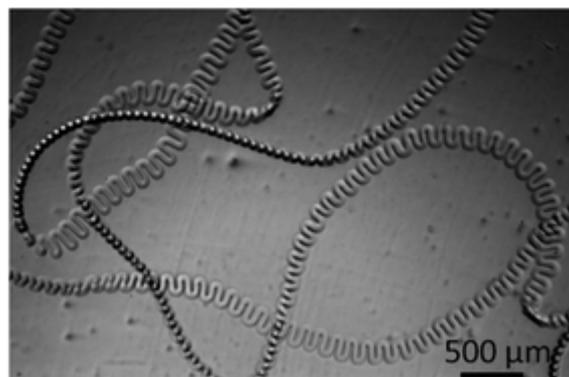


There is an abundance of experiments and theories on the glass transition of colloidal systems consisting of spherical particles. Much less is known about possible glass transitions in suspensions of rod-like colloids. In this study we present observations of a glass transition in suspensions of very long and thin rod-like, highly charged colloids. We use as a model system fd-virus particles (a DNA strand covered with coat proteins) at low ionic strength, where thick electric double layers are present. Structural arrest as a result of particle-caging is observed by means of dynamic light scattering. The glass-transition concentration is found to be far above the isotropic–nematic coexistence region. The morphology of the system thus consists of nematic domains with different orientations. Below the glass-transition concentration the initial morphology with large shear-aligned domains breaks up into smaller domains, and equilibrates after typically 50–100 hours. We quantify the dynamics of the transitional and the equilibrated texture by means of image time-correlation. A sharp increase of relaxation times of image time-correlation functions is found at the glass-transition concentration. The texture dynamics thus freezes at the same concentration where structural arrest occurs. We also observe a flow instability, which sets in after very long waiting times (typically 200–300 hours), depending on the rod concentration, which affects the texture morphology.

- Microfluidic tailoring of the two-dimensional morphology of crimped microfibers

Nunes, J. K.; Constantin, H.; Stone, H. A. *Soft Matter* **2013**, *9*, 4227-4235.

Abstract:



We synthesized uniform crimped microfibers with controlled dimensions using a microfluidic approach, whereby a liquid jet flows from a narrow channel into a wider channel. The liquid jet, sheathed by an immiscible non-reacting liquid, undergoes ultraviolet (UV)-initiated gelation upstream of the channel widening. At the channel widening, the reacting jet may buckle due to an axial

compressive stress, and the transient buckled morphology is preserved in the structure of the resulting solid fiber as the gelation reaction rapidly goes to completion. We investigated the effects of different experimental conditions, such as flow rate, UV light position, concentration of photoinitiator and UV light intensity on controlling the morphology of the microfibers, and we observed that the degree of crimp in the microfiber is dependent mainly on the extent of reaction.