The effect of isotopic substitution on the chirality of a self-assembled helix.
Cantekin, S.; Balkenende, D. W. R.; Smulders, M. M. J.; Palmans, A. R. A.; Meijer, E. W. 1
Nature Chemistry 2011, 3, 42-46.
<u>Abstract:</u>



N,N',N''-trialkylbenzene-1,3,5-tricarboxamides (BTAs) self-assemble by means of strong, threefold α -helix-type intermolecular hydrogen bonding into well-defined, helical, one-dimensional columnar aggregates. When a stereogenic centre is introduced into the alkyl side chains of these BTAs, strong Cotton effects are observed in dilute apolar solutions, indicating the preference for one helical conformation over the other. Here, we report the creation of a helical sense preference in self-assembled BTAs by introducing deuterium/hydrogen isotope chirality into the alkyl side chains. We determine the relative stabilities of the left- and right-handed helical conformations of these deuterated supramolecular polymers by performing a conformational analysis. Our findings show that the results of deuterium/hydrogen substitution in BTA-based supramolecular polymers and helical polyisocyanates are very similar, although the formation mechanisms differ. The selectively deuterated BTAs discussed here represent the first example of supramolecular chirality resulting from isotope substitution.

Supracolloidal Reaction Kinetics of Janus Spheres
Chen, Q.; Whitmer, J. K.; Jiang, S.; Bae, S. C.; Luijten, E.; Granick, S. Science 2011, 331, 199-202.





Clusters in the form of aggregates of a small number of elemental units display structural, thermodynamic, and dynamic properties different from those of bulk materials. We studied the kinetic pathways of self-assembly of "Janus spheres" with hemispherical hydrophobic attraction and found key differences from those characteristic of molecular amphiphiles. Experimental visualization combined with theory and molecular dynamics simulation shows that small, kinetically favored isomers fuse, before they equilibrate, into fibrillar triple helices with at most six nearest neighbors per particle. The time scales of colloidal rearrangement combined with the directional interactions resulting from Janus geometry make this a prototypical system to elucidate, on a mechanistic level and with single-particle kinetic resolution, how chemical anisotropy and reaction kinetics coordinate to generate highly ordered structures.

Interfacing Strong Electron Acceptors with Single Wall Carbon Nanotubes
Oelsner, C.; Schmidt, C.; Hauke, F.; Prato, M.; Hirsch, A.; Guldi, D. M. J. Am. Chem. Soc. 2011, 133, 4580-4586.

Abstract:



The complementary use of steady-state and time-resolved spectroscopy in combination with electrochemistry and microscopy are indicative of mutual interactions between semiconducting SWNTs and a water-soluble strong electron acceptor, i.e., perylenediimide. Significant is the stability and the strong electronic coupling of the perylenediimide/SWNT electron donor-acceptor hybrids. Several spectroscopic and spectroelectrochemical techniques, i.e., Raman, absorption, and fluorescence, confirmed that distinct ground- and excited-state interactions occur and that kinetically and spectroscopically well characterized radical ion pair states form within a few picoseconds..

Bulk Heterojunction Solar Cells Using Thieno[3,4-c]pyrrole-4,6-dione and Dithieno[3,2-b:2',3'-d]silole Copolymer with a Power Conversion Efficiency of 7.3%
Chu, T.-Y.; Lu, J.; Beaupré, S.; Zhang, Y.; Pouliot, J.-R.; Wakim, S.; Zhou, J.; Leclerc, M.; Li, Z.; Ding, J.; Tao, Y. J. Am. Chem. Soc. 2011, 133, 4250-4253.
<u>Abstract:</u>



A new alternating copolymer of dithienosilole and thienopyrrole-4,6-dione (PDTSTPD) possesses both a low optical bandgap (1.73 eV) and a deep highest occupied molecular orbital energy level (5.57 eV). 3 The introduction of branched alkyl chains to the dithienosilole unit was found to be critical for the improvement of the polymer solubility. When blended with $PC_{71}BM$, PDTSTPD exhibited a power conversion efficiency of 7.3% on the photovoltaic devices with an active area of 1 cm².

Programming the Supramolecular Helical Polymerization of Dendritic Dipeptides via the Stereochemical Information of the Dipeptide Rosen, B. M.; Peterca, M.; Morimitsu, K.; Dulcey, A. E.; Leowanawat, P. T.; Resmerita, A. M.; Imam, M. R.; Percec, V. J. Am. Chem. Soc. 2011, 133, 5135–5151.
<u>Abstract:</u>



Many natural biomacromolecules are homochiral and are built from constituents possessing identical handedness. The construction of synthetic molecules, macromolecules, and supramolecular structures with tailored stereochemical sequences can detail the relationship between chirality and function and provide insight into the process that leads to the selection of handedness and amplification of chirality. Dendritic dipeptides, previously reported from our laboratory, selfassemble into helical porous columns and serve as fundamental mimics of natural porous helixforming proteins and supramolecular polymers. Herein, the synthesis of all stereochemical permutations of a self-assembling dendritic dipeptide including homochiral, heterochiral, and differentially racemized variants is reported. A combination of CD/UV-vis spectroscopy in solution and in film, X-ray diffraction, and differential scanning calorimetry studies in solid state established the role of the stereochemistry of the dipeptide on the thermodynamics and mechanism of selfassembly. It was found that the highest degree of stereochemical purity, enantiopure homochiral dendritic dipeptides, exhibits the most thermodynamically favorable self-assembly process in solution corresponding to the greatest degree of helical order and intracolumnar crystallization in solid state. Reducing the stereochemical purity of the dendritic dipeptide through heterochirality or by partially or fully racemizing the dendritic dipeptide destructively interferes with the self-assembly process. All dendritic dipeptides were shown to coassemble into single columns regardless of their stereochemistry. Because these columns exhibit no deracemization, the thermodynamic advantage of enantiopurity and homochirality suggests a mechanism for stereochemical selection and chiral amplification.

 Accumulative Charge Separation Inspired by Photosynthesis Karlsson, S.; Boixel, J.; Pellegrin, Y.; Blart, E.; Becker, H.-C.; Odobel, F.; Hammarstrom, L. J. Am. Chem. Soc. 2010, 132, 17977–17979.
<u>Abstract:</u>



Molecular systems that follow the functional principles of photosynthesis have attracted increasing attention as a method for the direct production of solar fuels. This could give a major carbon-neutral energy contribution to our future society. An outstanding challenge in this research is to couple the light-induced charge separation (which generates a single electron-hole pair) to the multielectron processes of water oxidation and fuel generation. New design considerations are needed to allow for several cycles of photon absorption and charge separation of a single artificial photosystem. Here we demonstrate a molecular system with a regenerative photosensitizer that shows two successive events of light-induced charge separation, leading to high-yield accumulation of redox equivalents on single components without sacrificial agents.

 Synthesis and Binding Studies of Novel Diethynyl-Pyridine Amides with Genomic Promoter DNA G-Quadruplexes
Dash, J.; Waller, Z. A. E.; Panto, G. D.; Balasubramanian, D. S. Chem.Eur. J. 2011, 17, 4571– 4581.
<u>Abstract:</u>



Herein, we report the design, synthesis and biophysical evaluation of novel 1,2,3-triazole-linked diethynyl-pyridine amides and trisubstituted diethynyl-pyridine amides as promising G-quadruplex binding ligands. We have used a Cul-catalysed azide–alkyne cycloaddition click reaction to prepare the 1,2,3-triazole-linked diethynyl-pyridine amides. The G-quadruplex DNA binding properties of the ligands have been examined by using a Förster resonance energy transfer (FRET) melting assay and surface plasmon resonance (SPR) experiments. The investigated compounds are conformationally flexible, having free rotation around the triple bond, and exhibit enhanced G-quadruplex binding stabilisation and specificity between intramolecular promoter G-quadruplex DNA motifs compared to the first generation of diarylethynyl amides (J. Am. Chem. Soc.2008, 130, 15950–15956). The ligands show versatility in molecular recognition and promising G-quadruplex discrimination with 2–50-fold selectivity exhibited between different intramolecular promoter G-quadruplexes. Circular dichroism

(CD) spectroscopic analysis suggested that at higher concentration these ligands disrupt the c-kit2 Gquadruplex structure. The studies validate the design concept of the 1,3-diethynyl-pyridine-based scaffold and demonstrate that these ligands exhibit not only significant selectivity over duplex DNA but also variation in G-quadruplex interaction properties based on small chemical changes in the scaffold, leading to unprecedented differential recognition of different DNA G-quadruplex sequences.

 Amine Exchange in Formamidines: An Experimental and Theoretical Study Capela, M.; Mosey, N. J.; Xing, L.; Wang, R.; Petitjean, A. *Chem.Eur. J.* 2011, *17*, 4598–4612. <u>Abstract:</u>



N — H-containing formamidines combine a reasonably strong association to carboxylic acids to form complexes of well-defined geometries with a simultaneous proton-induced electrophilicity enhancement that allows for the exchange of their amine portion. The N = C(H) — NH fragment, therefore, undergoes "imine-like" exchange with N-containing nucleophiles. Because of the prototropic equilibrium, the N = C(H) — NH fragment may behave as a "bisimine" centred on the same carbon, in which both N-containing fragments can be exchanged. Considering the proton-induced sensitisation of both C — N units and the well-defined formamidine–carboxylic acid complex geometry, it should be possible to use carboxylic acids as templates for the synthesis of defined architectures by dynamic amine exchange within formamidines. This study highlights three exchange regimes based on the nature of the incoming amine (aliphatic amines, aromatic amines and alkoxyamines), as well as exchange rules based on the amine leaving groups. Following this analysis, a proof of concept for carboxylic acid templated macrocycle formation through dynamic exchange is provided.

 Direct observation of stepwise movement of a synthetic molecular transporter Wickham, S. F. J.; Endo, M.; Katsuda, Y.; Hidaka, K.; Bath, J.; Sugiyama, H.; Turberfield, A. J. *Nature. Nanotech.* 2011, *6*, 166–169. Abstract:

> a 100 mb 1 m 100 m

Controlled motion at the nanoscale can be achieved by using Watson–Crick base-pairing to direct the assembly and operation of a molecular transport system consisting of a track, a motor1 and fuel, all made from DNA. Here, we assemble a 100-nm-long DNA track on a two-dimensional scaffold, and show that a DNA motor loaded at one end of the track moves autonomously and at a constant average speed along the full length of the track, a journey comprising 16 consecutive steps for the motor. Real-time atomic force microscopy allows direct observation of individual steps of a single motor, revealing mechanistic details of its operation. This precisely controlled, long-range transport could lead to the development of systems that could be programmed and routed by instructions encoded in the nucleotide sequences of the track and motor. Such systems might be used to create molecular assembly lines modelled on the ribosome.

• J-Aggregates: From Serendipitous Discovery to Supramolecular Engineering of Functional Dye Materials

Würthner, F.; Kaiser, T. E.; Saha-Möller, C. R. Angew. Chem. Int. Ed. **2011**, 50, 3376–3410. Abstract:



After more than 75 years since their discovery, J-aggregates are continuing to be of great interest. This Review provides an overview on J-aggregates of various classes of dyes, including cyanines, porphyrins, phthalocyanines, and perylene bisimides, with specific emphasis on supramolecular construction principles, optical properties, and perspectives for applications.

J-aggregates are of significant interest for organic materials conceived by supramolecular approaches. Their discovery in the 1930s represents one of the most important milestones in dye chemistry as well as the germination of supramolecular chemistry. The intriguing optical properties of J-aggregates (in particular, very narrow red-shifted absorption bands with respect to those of the monomer and their ability to delocalize and migrate excitons) as well as their prospect for applications have motivated scientists to become involved in this field, and numerous contributions have been published. This Review provides an overview on the J-aggregates of a broad variety of dyes (including cyanines, porphyrins, phthalocyanines, and perylene bisimides) created by using supramolecular construction principles, and discusses their optical and photophysical properties as well as their potential applications. Thus, this Review is intended to be of interest to the supramolecular, photochemistry, and materials science communities.

Responsive Vesicles from Dynamic Covalent Surfactants
Minkenberg, C. B.; Li, F.; van Rijn, P.; Florusse, L.; Boekhoven, J.; Stuart, M. C. A.; Koper, G. J. M.; Eelkema, R.; van Esch, J. H. Angew. Chem. Int. Ed. 2011, 50, 3421–3424.
<u>Abstract:</u>



Breaking bilayers: Incorporation of dynamic covalent bonds in vesicle-forming surfactants leads to the formation of responsive vesicles, which can be switched back and forth between the bilayer state and the isotropic solution using either dilution or a change in the pH value as external stimuli.

• Amphiphilic porphyrin assembly as a highly selective chemosensor for organic mercury in water

Liu, B.-W.; Chen, Y.; Song, B.-E.; Liu, Y. *Chem. Commun.* **2011**, *47*, 4418-4420. <u>Abstract:</u>



Homogeneously sized nanoparticles were successfully constructed based on amphiphilic porphyrincholesterol arrays, showing unique spectral and colourimetric response to organic mercury in water, even in the presence of Hg²⁺.

• Self-assembled nanospheres as a novel delivery system for taxol: a molecular hydrogel with nanosphere morphology

Wang, H.; Yang, C.; Wang, L.; Kong, D.; Zhang, Y.; Yang, Z. <u>Chem. Commun.</u> **2011**, 47, 4439-4441.

Abstract:



A molecular hydrogel based on a Folate–Taxol conjugate was reported in this study.

• Preparation and characterization of temperature-responsive and magnetic nanomicelles Huang, C.; Zhou, Y.; Jin, Y.; Zhou, X.; Tang, Z.; Guo, X.; Zhou, S. J. Mater. Chem. **2011**, *21*, 5660-5670.



One type of the temperature-responsive and magnetic nanomicelles was synthesized based on SPIONs (superparamagnetic iron oxide nanoparticles) and the biocompatible polymer-Pluronic F127 or its copolymer with poly(DL-lactic acid) (F127-PLA) via a facile chemical conjugation method. The magnetic nanomicelles were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), a vibrating sample magnetometer (VSM), dynamic light scattering measurements (DLS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The varying volume shrinkage of the magnetic nanomicelles was detected when increasing the temperature from 15 to 45 °C. Doxorubicin hydrochloride (DOX·HCI) was selected as a model anticancer drug to investigate the drug loading and release behavior in the buffer solutions with different pH values and in an alternating magnetic field (MF). The Alamar blue assay was performed to evaluate the biocompatibility of the micelles and the antiproliferative effect of the drug-loaded micelles. The results displayed that the magnetic micelles were safe carriers and the DOX HCI-loaded micelles were equally effective as the free drug for suppressing the growth of tumor cells. The blood compatibility studies showed few effects on coagulation and hemolysis. Therefore, the magnetic micelles possess many great potential applications in the field of nanomedicine.

 Folate-conjugated crosslinked biodegradable micelles for receptor-mediated delivery of paclitaxel

Xiong, J.; Meng, F.; Wang, C.; Cheng, R.; Liu, Z.; Zhong, Z. J. Mater. Chem. **2011**, *21*, 5786-5794.

Abstract:



The poor stability of micellar drug delivery systems *in vivo* due to large volume dilution and interactions with blood pool often leads to premature drug release with low targetability and therapeutic efficacy. Here, we designed folate-conjugated interfacially crosslinked biodegradable micelles consisting of poly(ethylene glycol)-*b*-poly(acryloyl carbonate)-*b*-poly(D,L-lactide) (PEG-PAC-PLA) and folate-PEG-PLA (FA-PEG-PLA) block copolymers for receptor-mediated delivery of paclitaxel

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(PTX) into KB cells. Micelles with varying amounts of folate ligands were prepared at 0–20 wt.% of FA-PEG-PLA. The resulting micelles, either with or without PTX loading, were readily crosslinked by UV irradiation. The crosslinked micelles had much smaller sizes and better stability as compared to the non-crosslinked controls. Notably, these micelles achieved high drug loading efficiencies of 70–88% at an initial PTX loading content of 10 wt.%. The *in vitro* release studies revealed that crosslinked micelles exhibited significantly inhibited PTX release at low micelle concentrations. MTT assays in KB cells showed that the crosslinked micelles were non-toxic while the toxicity of PTX-loaded micelles, either crosslinked or non-crosslinked, increased with increasing folate contents. Remarkably, at 12 h incubation time folate-decorated PTX-loaded crosslinked micelles composed of 20 wt.% of FA-PEG-PLA displayed markedly higher toxicity to KB cells than free PTX (33% *versus* 50% cell viability), which is most likely due to their much more efficient cellular uptake through FA receptor-mediated endocytosis. Flow cytometry studies showed that folate-decorated FITC-labeled crosslinked micelles were much more efficiently taken up by KB cells than controls without folate ligands. These results indicate that ligand-conjugated interfacially crosslinked PEG-PLA micelles have great potential in targeted cancer therapy.

Advances in the field of π-conjugated 2,2':6',2"-terpyridines
Wild, A.; Winter, A.; Schlütter, F.; Schubert, U. S. *Chem. Soc. Rev.* 2011, 40, 1459–1511.
<u>Abstract:</u>



This *critical review* summarizes the research progress made in the field of π -conjugated terpyridines within the last decade. Supramolecular materials based on metal ion complexes of 2,2 :6 ,2 - terpyridine derivatives have found manifold potential applications—from opto-electronic devices to life science. In this contribution, synthetic strategies towards π -conjugated terpyridines and their incorporation into advanced supramolecular architectures are evaluated. Applications as photoactive species in, *e.g.*, photovoltaic devices, polymer light-emitting diodes (PLEDSs) and nanotechnology are discussed comprehensively (523 references).

 Sensitizer molecular structure-device efficiency relationship in dye sensitized solar cells Clifford, J. N.; Martínez-Ferrero, E.; Viterisi, A.; Palomares, E. Chem. Soc. Rev. 2011, 40, 1635–1646.
Abstract:

Abstract:



In the Dye Sensitized Solar Cell (DSSC) the dye sensitizer carries out the light harvesting function and is therefore crucial in determining overall cell efficiency. In addition, the dye sensitizer can influence many of the key electron transfer processes occurring at the $TiO_2/dye/electrolyte$ interface which also determine efficiency. Dye structure can influence and drive forward electron injection into the conduction band of the TiO_2 . Conversely, dye structure can help retard loss electron transfer processes such as charge recombination of injected electrons in the TiO_2 with dye cations and also recombination of these electrons with the electrolyte. Therefore tuning dye sensitizer light absorbing properties and control of the aforementioned electron transfer processes through structural design of the dye sensitizer is an important avenue through which optimization of DSSC efficiency should be pursued. In this *critical review* the latest work focusing on the design of dyes for efficient DSSCs is revised (111 references).

 Substituted 1,3-Bis(imino)isoindole Diols: A New Class of Proton Transfer Dyes Hanson, K.; Patel, N.; Whited, M. T. P.; Djurovich, I.; Thompson, M. E. Org. Lett. 2011, 13, 1598–1601.
<u>Abstract:</u>



A new class of excited-state intramolecular proton transfer (ESIPT) dyes based on a 1,3bis(imino)isoindole diol motif has been prepared. These molecules exhibit orange emission (600 nm) with a large apparent Stokes shift (>6000 cm⁻¹) and quantum efficiencies up to 45%. Selective modification of the substitutents can be used to shift the equilibrium between the enol and keto forms of the molecule in both the ground and excited states.

 Encapsulation of Tetrathiafulvalene Inside a Dimeric Molecular Capsule Qiu, Y.; Yi, S.; Kaifer, A. E. *Org. Lett.* **2011**, *13*, 1770–1773.
<u>Abstract:</u>



Tetrathiafulvalene (TTF) is trapped inside a dimeric capsule formed by two octaacid, deep-cavity cavitands in aqueous solution. While the first one-electron oxidation of TTF is strongly hindered by 11 encapsulation, the capsular assembly is eventually destabilized upon oxidation of the guest.

• Reversible Imine Shell Cross-Linked Micelles from Aqueous RAFT-Synthesized Thermoresponsive Triblock Copolymers as Potential Nanocarriers for "pH-Triggered" Drug Release

Xu, X.; Flores, J. D.; McCormick, C. L. *Macromolecules* **2011**, *44*, 1327–1334. <u>Abstract:</u>



A temperature-responsive triblock copolymer, α -methoxypoly(ethylene oxide)-b-poly(N-(3aminopropyl)methacrylamide)-*b*-poly(*N*-isopropylacrylamide) (mPEO-PAPMA-PNIPAM), was synthesized via aqueous RAFT (aRAFT) polymerization. At room temperature, the polymer is hydrophilic and exists as unimers in aqueous solution. Increasing the solution temperature above the lower critical solution temperature (LCST) of the PNIPAM block leads to self-assembly into micelles with PNIPAM cores, PAPMA shells, and mPEO coronas with hydrodynamic diameter (D_h) values of ca. 52 nm. The PAPMA shell was cross-linked with terephthaldicarboxaldehyde (TDA) at pH 9.0 to generate shell cross-linked (SCL) micelles with cleavable imine linkages. The reversible pH- and temperature-dependent formation and cleavage of the (SCL) micelles was followed by dynamic light scattering and NMR spectroscopy. As well, the release of the model hydrophobic drug prednisolone 21-acetate (PA) from loaded SCL micelles was studied at specific pH and temperature conditions. PA was released at pH < 6.0 as hydrolytic cleavage of the imine cross-links within the swollen SCL micelles occurred. Such "pH-triggered" release behavior conceptually demonstrates that the reversible SCL micelles prepared by this simple procedure from temperature-responsive triblock copolymers have promise as therapeutic nanocarriers in biomedicine.

 Cyclodextrin-Modified Polyesters from Lactones and from Bacteria: An Approach to New Drug Carrier Systems

Jazkewitsch, O.; Mondrzyk, A.; Staffel, R.; Ritter, H. *Macromolecules* **2011**, *44*, 1365–1371. <u>Abstract:</u>



Copper(I)-catalyzed cycloaddition of synthetic and bacterial copolyesters bearing pendant alkyne group with mono-(6-azido-6-desoxy)- β -cyclodextrin was carried out to synthesize β -CD-functionalized copolyester. The synthetic "clickable" copolyesters were obtained by the ring-opening copolymerization of the propargyl-modified lactones and ϵ -caprolactone. The bacterial copolyesters containing an alkyne group were biosynthesized from a mixture of 10-undecynoic acid and hexanoic acid by the Gram-negative bacteria *Pseudomonas oleovorans*. The modified products of the "click"

reaction were characterized by FT-IR, ¹H NMR spectroscopy, and DSC. Furthermore, the host guest capability of covalently attached β -cyclodextrin moieties was proved by dynamic light scattering 12 measurements.

Super Gas Barrier of All-Polymer Multilayer Thin Films
Yang, Y.-H.; Haile, M.; Park, Y. T.; Malek, F. A.; Grunlan, J. C. *Macromolecules* 2011, 44, 1450–1459.

Abstract:



Thin film assemblies of branched polyethylenimine (PEI) and poly(acrylic acid) (PAA), deposited using the layer-by-layer technique, were studied in an effort to produce all-polymer thin films with low oxygen permeability. Altering the pH of PEI and PAA results in large thickness variations (from 90 nm to 4.74 µm for 30-bilayer films). Cross-linking these films with glutaraldehyde (GA) create an inhibition of polymer interdiffusion, causing exponential film growth to be reset. AFM images show the surface morphology of PEI/PAA assemblies can be controlled by the pH and the final polymer layer deposited, with surface roughness ranging from 2.1 to 49.1 nm. Most pH combinations failed to produce a film with high oxygen barrier, but 8 bilayers of PEI at pH 10 and PAA at pH 4 produce a 305 nm thick film with an oxygen transmission rate below 0.005 cm³/(m² day). This unique thin film barrier ($P_{02} < 3.2 \times 10^{-21}$ cm³ (STP) cm/(cm² s Pa)) is a promising alternative to current polymeric membranes, flexible electronics, and food packaging materials.

• A Physical and Mechanical Study of Prestressed Competitive Double Network Thermoplastic Elastomers

Singh, N. K.; Lesser, A. J. *Macromolecules* **2011**, *44*, 1480–1490. <u>Abstract:</u>



A new approach to prepare and characterize prestressed competitive double network elastomeric systems was investigated. A styrene–butadiene–styrene (SBS) triblock copolymer system containing physical cross-links was used to achieve a double network by additional chemical cross-linking using ultraviolet (UV) light. Properties measured from conventional monotonic tensile tests, stress relaxation, thermomechanical, hysteresis, and swelling analysis were investigated and related to their network structure. These double network elastomers show a transition between competitive and collaborative behavior in their mechanical properties at different strain regimes. These elastomers also show lower permanent set in both low and high strain regimes along with lower

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hysteresis. These networks exhibit lower modulus along with lower coefficient of thermal expansion, still showing lower swelling ratios, which results from a competition between the networks. 13
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