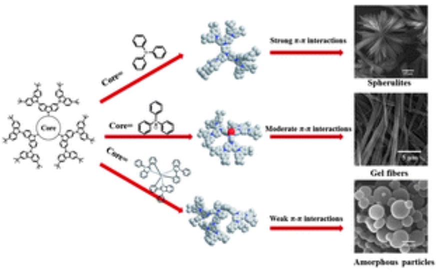
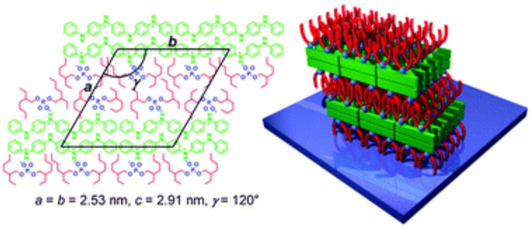
- Supramolecular assemblies from carbazole dendrimers modulated by core size and molecular configuration
  Ding, Z.; Xing, R.; Wang, X.; Ding, J.; Wang, L.; Han, Y. *Soft Matter* **2013**, *9,* 11404-11412.
  Abstract:



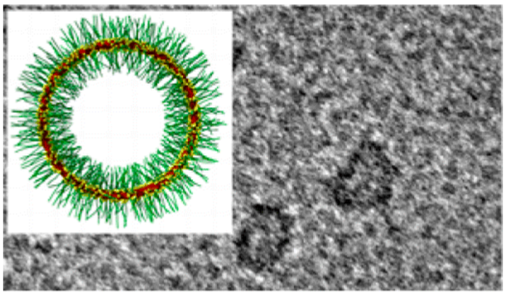
Different core moieties can modulate the self-assembly behaviors of second generation carbazole-based conjugated dendrimers with the same dendrons and surface groups in a solvent mixture of a good solvent and an anti-solvent. For TA-D2 with triphenylamine as the core, crystalline spherulites were formed since the more planar molecular configuration of TA-D2 can enhance the ⍰–⍰ interactions between the carbazole dendrimers. For G2 with the large-sized *fac*-Ir(PBI)$_3$ as the core, amorphous globular particles were obtained because the large core in G2 increases the distance between carbazole dendrimers and decreases the π–π interactions. While for TPO-D2 with triphenylphosphine oxide as the core with moderate size and a twisted molecular configuration, a supramolecular gel consisting of fibers was formed in the solvent mixture of aromatic solvent and alcohol solvent. The sol–gel conversion of TPO-D2 can be observed by simple heating and cooling. Fast cooling and ultrasonication are beneficial to get uniform TPO-D2 gel with small aggregates. The TPO-D2 xerogel shows three-dimensional networks with the nanofibers entangling and intersecting with each other. The moderate π–π interactions between the carbazole units modulated by the core may be the driving force for TPO-D2 to form the gel, the balance phase between the ordered crystal and amorphous precipitate.

- Oligo(aniline) nanofilms: from molecular architecture to microstructure
  Dane, T. G.; Cresswell, P. T.; Pilkington, G. A.; Lilliu, S.; Macdonald, J. E.; Prescott, S. W.; Bikondoa, O.; Faul, C. F. J.; Briscoe, W. H. *Soft Matter* **2013**, *9,* 10501-10511.
  Abstract:



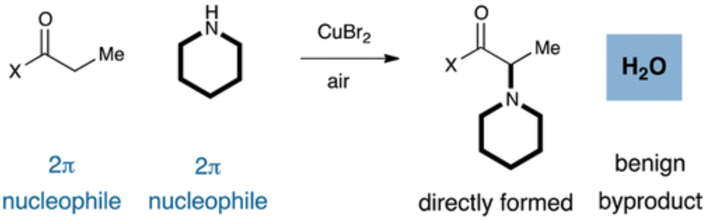
The self-assembly behaviour, structure, and consequently the electronic properties of electroactive organic molecules can differ significantly from those of the bulk material when confined to thin films. Here we have examined the self-organised in-plane and out-of-plane structures of aniline oligomers in thin films using surface-sensitive grazing-incidence X-ray scattering (GIXS). Thin films of the aniline tetramer (TANI) and octamer (OANI) were prepared both in their native emeraldine base (EB) oxidation state and in the doped emeraldine salt (ES) state (combined with the acid surfactant bis(ethyl hexyl)phosphate (BEHP)), using a simple drop-casting and solvent annealing process. It was found that the presence of the acid surfactant induced self-organisation into highly ordered structures. The details of these structures, such as the morphology, orientation relative to the underlying substrate and the degree of orientation were found to depend on the molecular architecture of the oligomer. The BEHP-doped TANI system formed a highly oriented hexagonal unit cell (lattice parameters: $a = b = 2.53$ nm, $c = 2.91$ nm, $\gamma = 120$), whereas the BEHP-doped OANI complex adopted a randomly oriented lamellar structure (*d*-spacing = 2.25 nm). Such detailed structural information reveals that the self-assembly behaviour and the packing of oligomer–BEHP complexes, when confined to thin films, are indeed different to that of the bulk phase materials. Furthermore, the molecular architecture of the oligomers directly influenced the structural changes of the doped films in response to in situ thermal treatment. These results demonstrate that through a simple processing route the morphology of electroactive oligomer films can be tailored by molecular design. These findings are important to future applications where thin film structure is a crucial consideration for device function and performance.

- Metallo-Supramolecular Cyclic Polymers
  Zhang, K.; Zha, Y.; Peng, B.; Chen, Y.; Tew, G. N. *J. Am. Chem. Soc.* **2013**, *135*, 15994–15997.
  Abstract:



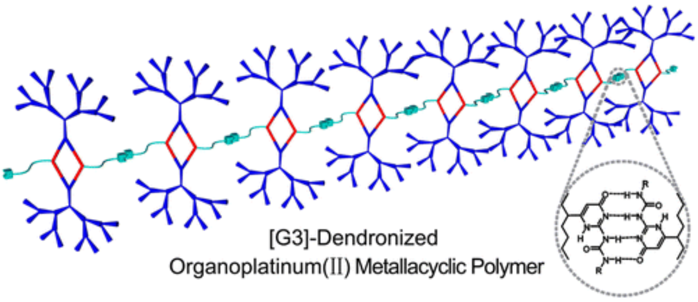
Cyclic brush polymers represent an exciting new macromolecular topology. For the first time, this new topology has been combined with metallo-supramolecular interactions to construct novel cyclic brush polymers. Here, ring-expansion metathesis polymerization was used to synthesize a universal cyclic template with a polynorbornene backbone, which was further modified with the metal-chelating synthon terpyridine. The terpyridine side chains served as the key supramolecular unit for the creation of cyclic polymer brushes and gels. This metallo-supramolecular functionality allowed direct visualization of the cyclic brush polymers by transmission electron microscopy for the first time. This demonstration should open a new area in which supramolecular interactions are used to build an array of novel cyclic brush copolymers as well as other cyclic-polymer-based architectures generating new materials.

- Simple Catalytic Mechanism for the Direct Coupling of α-Carbonyls with Functionalized Amines: A One-Step Synthesis of Plavix
  Evans, R. W.; Zbieg, J. R.; Zhu, S.; Li, W.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2013**, *135*, 16074–16077.
  Abstract:



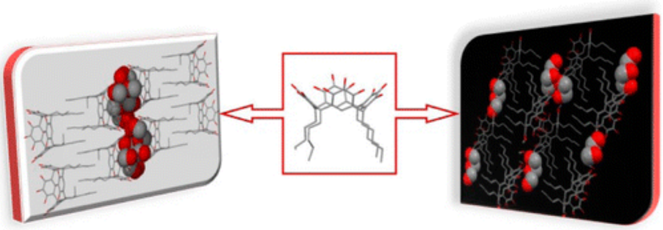
The direct α-amination of ketones, esters, and aldehydes has been accomplished via copper catalysis. In the presence of catalytic copper(II) bromide, a diverse range of carbonyl and amine substrates undergo fragment coupling to produce synthetically useful α-amino-substituted motifs. The transformation is proposed to proceed via a catalytically generated α-bromo carbonyl species; nucleophilic displacement of the bromide by the amine then delivers the α-amino carbonyl adduct while the catalyst is reconstituted. The practical value of this transformation is highlighted through one-step syntheses of two high-profile pharmaceutical agents, Plavix and amfepramone.

- Dendronized Organoplatinum(II) Metallacyclic Polymers Constructed by Hierarchical Coordination-Driven Self-Assembly and Hydrogen-Bonding Interfaces
  Yan, X.; Jiang, B.; Cook, T. R.; Zhang, Y.; Li, J.; Yu, Y.; Huang, F.; Yang, H.-B.; Stang, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 16813-16816.
  Abstract:



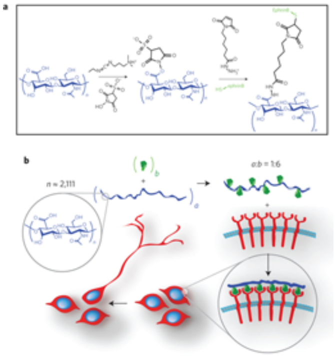
We describe the efficient preparation of rhomboidal metallacycles that self-assemble upon mixing a donor decorated with 2-ureido-4-pyrimidinone (UPy) with acceptors containing pendant [G1]-[G3] dendrons. The formed rhomboids subsequently polymerize into dendronized organoplatinum(II) metallacyclic polymers through H-bonding UPy interfaces, which possess the structural features of conventional dendronized polymers as well as the dynamic reversibility of supramolecular polymers. Preservation of both properties in a single material is achieved by exploiting hierarchical self-assembly, namely the unification of coordination-driven self-assembly with H-bonding, which provides facile routes to dendronized metallacycles and subsequent high ordering. The supramolecular polymerization defined here represents a novel method to deliver architecturally complex and ordered polymeric materials with adaptive properties.

- Pyrogallol[4]arenes as Frustrated Organic Solids
  Kumari, H.; Erra, L.; Webb, A. C.; Bhatt, P.; Barnes, C. L.; Deakyne, C. A.; Adams, J. E.; Barbour, L. J.; Atwood, J. L. *J. Am. Chem. Soc.* **2013**, *135*, 16963-16967.
  Abstract:



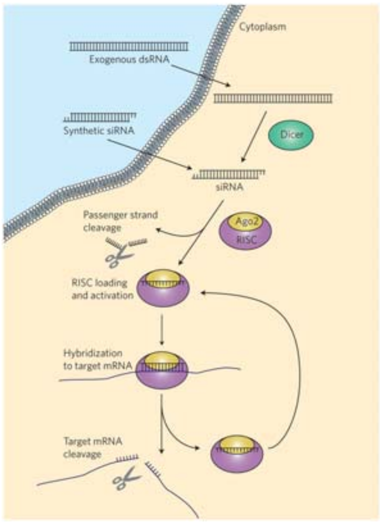
Two forms of interdigitated layered arrangements of C-pentylpyrogallol[4]arene (PgC_5) have been structurally elucidated and show variations in packing arrangements and host-guest interactions. Molecular dynamics simulations reveal a propensity for formation of self-included dimers, with or without incorporated solvent. Combined gas sorption and PXRD results show the presence of seven forms of PgC_5, with and without CO_2 (and their interconversions). This is the first CO_2 gas sorption study of pyrogallol[4]arenes, and it provides evidence that pyrogallol[4]arenes may act as frustrated organic solids.

- Multivalent ligands control stem cell behaviour *in vitro* and *in vivo*
  Conway, A.; Vazin, T.; Spelke, D. P.; Rode, N. A.; Healy, K. E.; Kane, R. S.; Schaffer, D. V. *Nature Nanotech.* **2013**, *8*, 831–838.
  Abstract:



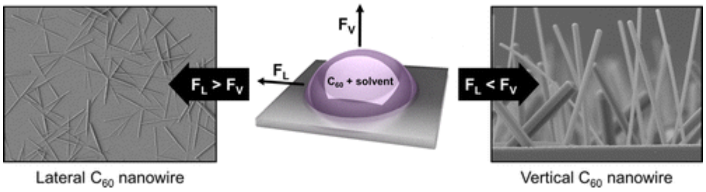
There is broad interest in designing nanostructured materials that can interact with cells and regulate key downstream functions. In particular, materials with nanoscale features may enable control over multivalent interactions, which involve the simultaneous binding of multiple ligands on one entity to multiple receptors on another and are ubiquitous throughout biology. Cellular signal transduction of growth factor and morphogen cues (which have critical roles in regulating cell function and fate) often begins with such multivalent binding of ligands, either secreted or cell-surface-tethered to target cell receptors, leading to receptor clustering. Cellular mechanisms that orchestrate ligand–receptor oligomerization are complex, however, so the capacity to control multivalent interactions and thereby modulate key signalling events within living systems is currently very limited. Here, we demonstrate the design of potent multivalent conjugates that can organize stem cell receptors into nanoscale clusters and control stem cell behaviour *in vitro* and *in vivo*. The ectodomain of ephrin-B2, normally an integral membrane protein ligand, was conjugated to a soluble biopolymer to yield multivalent nanoscale conjugates that potently induce signalling in neural stem cells and promote their neuronal differentiation both in culture and within the brain. Super-resolution microscopy analysis yielded insights into the organization of the receptor–ligand clusters at the nanoscale. We also found that synthetic multivalent conjugates of ephrin-B1 strongly enhance human embryonic and induced pluripotent stem cell differentiation into functional dopaminergic neurons. Multivalent bioconjugates are therefore powerful tools and potential nanoscale therapeutics for controlling the behaviour of target stem cells *in vitro* and *in vivo*.

- Delivery materials for siRNA therapeutics
  Kanasty, R.; Dorkin, J. R.; Vegas, A.; Anderson, D. *Nature Mater.* **2013**, *12*, 967–977.
  Abstract:



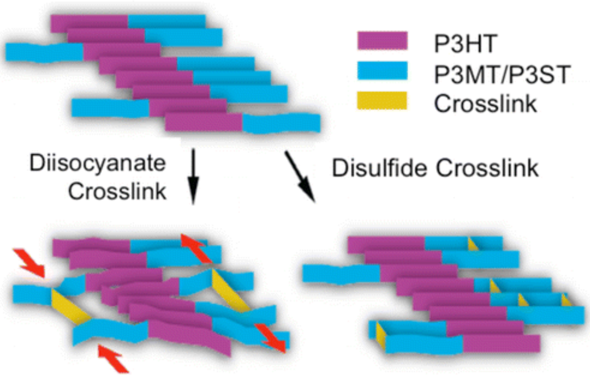
RNA interference (RNAi) has broad potential as a therapeutic to reversibly silence any gene. To achieve the clinical potential of RNAi, delivery materials are required to transport short interfering RNA (siRNA) to the site of action in the cells of target tissues. This Review provides an introduction to the biological challenges that siRNA delivery materials aim to overcome, as well as a discussion of the way that the most effective and clinically advanced classes of siRNA delivery systems, including lipid nanoparticles and siRNA conjugates, are designed to surmount these challenges. The systems that we discuss are diverse in their approaches to the delivery problem, and provide valuable insight to guide the design of future siRNA delivery materials.

- Vertical Crystallization of C60 Nanowires by Solvent Vapor Annealing Process
  Kim, J.; Park, C.; Park, J. E.; Chu, K.; Choi, H. C. *ACS Nano* **2013**, *7*, 9122–9128.
  <u>Abstract:</u>



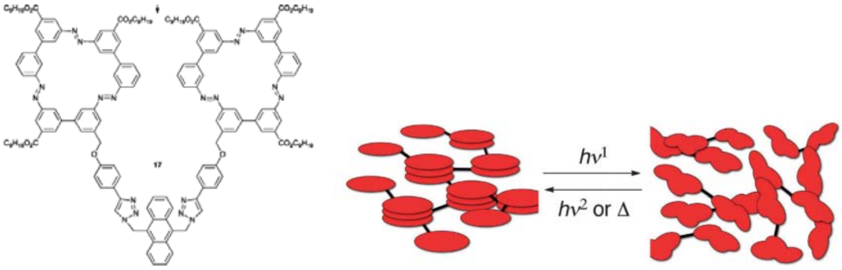
We report that C60 molecules are spontaneously crystallized into vertical nanowires by the solvent vapor annealing (SVA) process. C60 molecules have been known to be assembled into wire-like crystals by simply dropping and drying C60 solutions in m-xylene on a solid substrate. By the drop-drying process, C60 nanowires have been mostly grown laterally on a solid substrate, as the major force applied to the droplet during the drying process is parallel to the substrate. On the other hand, the SVA process seems to provide an ideal environment under which the direction of the dominant drying force of a droplet becomes vertical. When a thermally evaporated C60 film is exposed to m-xylene solvent vapor under controlled SVA environments at room temperature, C60 molecules are found to be crystallized into vertical nanowires. The effect of solvent vapor pressure on the vertical growth of C60 nanowire is examined by comparative studies using mesitylene and 1,3-dichlorobenzene. The versatility of the SVA process for the growth of vertical organic nanostructures is further demonstrated by the successful formations of vertically grown C60 2D disks and 5,7,12,14-pentacenetetrone anisotropic crystals by employing carbon tetrachloride and toluene solvent vapors, respectively.

- Cross-Linked Functionalized Poly(3-hexylthiophene) Nanofibers with Tunable Excitonic Coupling
  Baghgar, M.; Pentzer, E.; Wise, A. J.; Labastide, J. A.; Emrick, T.; Barnes, M. D. *ACS Nano* **2013**, *7*, 8917–8923.
  Abstract:



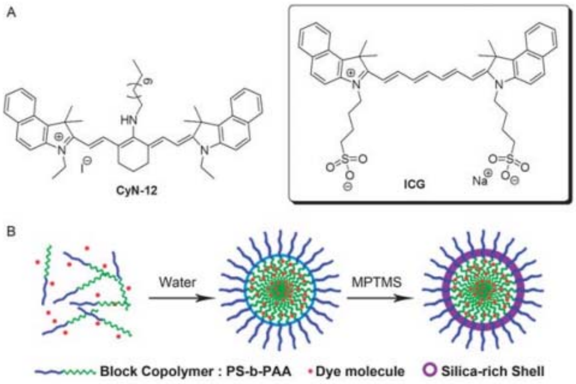
We show that mechanically and chemically robust functionalized poly(3-hexylthiophene) (P3HT) nanofibers can be made via chemical cross-linking. Dramatically different photophysical properties are observed depending on the choice of functionalizing moiety and cross-linking strategy. Starting with two different nanofiber families formed from (a) P3HT-b-P3MT or (b) P3HT-b-P3ST diblock copolymers, cross-linking to form robust nanowire structures was readily achieved by either a third-party cross-linking agent (hexamethylene diisocyanate, HDI) which links methoxy side chains on the P3MT system, or direct disulfide cross-link for the P3ST system. Although the nanofiber families have similar gross structure (and almost identical pre-cross-linked absorption spectra), they have completely different photophysics as signaled by ensemble and single nanofiber wavelength- and time-resolved photoluminescence as well as transient absorption (visible and near-IR) probes. For the P3ST diblock nanofibers, excitonic coupling appears to be essentially unchanged before and after cross-linking. In contrast, cross-linked P3MT nanofibers show photoluminescence similar in electronic origin, vibronic structure, and lifetime to unaggregated P3HT molecules, e.g., dissolved in an inert polymer matrix, suggesting almost complete extinction of excitonic coupling. We hypothesize that the different photophysical properties can be understood from structural perturbations resulting from the cross-linking: For the P3MT system, the DIC linker induces a high degree of strain on the P3HT aggregate block, thus disrupting both intra- and interchain coupling. For the P3ST system, the spatial extent of the cross-linking is approximately commensurate with the interlamellar spacing, resulting in a minimally perturbed aggregate structure.

- Switchable 3D networks by light controlled π-stacking of azobenzene macrocycles
  Reuter, R.; Wegner, H. A. *Chem. Commun.* **2013***, 49,* 146-148.
  Abstract:



Azobenzene macrocycles were designed for switchable π-stacking interaction. After efficient preparation and characterization of azobenzene macrocycles containing electron rich as well as electron poor elements a dimeric analogue was synthesized, which formed reversibly 3D-networks. Gel formation was observed with aromatic solvents representing the first example of this type based on switchable azobenzene macrocycles.

- Constructing NIR silica-cyanine hybrid nanocomposite for bioimaging in vivo: a breakthrough in photostability and bright fluorescence with large stokes shift
  Wu, X.; Chang, S.; Sun, X.; Guo, Z.; Li, Y.; Tang, J.; Shen, Y.; Shi, J.; Tian, H.; Zhu, W. *Chem. Sci.* **2013***, 4,* 1221-1228.
  Abstract:

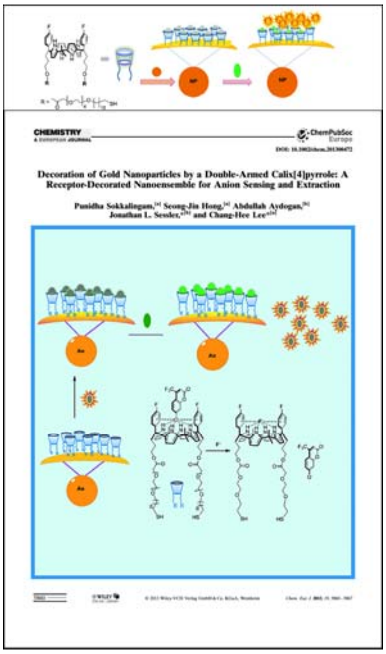


Optical near-infrared (NIR) nanomaterials provide a unique opportunity for applications in bioimaging and medical diagnosis. A kind of hydrophilic NIR fluorescent core-shell structured silica nanoparticle containing NIR cyanine chromophore, named as CyN-12@NHs, for in vivo bioimaging is developed through a facile one-pot strategy. The hydrophobic CyN-12 molecules can be successfully encapsulated into the core via the self-assembly of the amphiphilic block copolymer PS-b-PAA and subsequent shell cross-linking of silane. The as-prepared CyN-12@NHs exhibits typically spherical core-shell structure, which has a uniform size of 35 nm with a narrow size distribution, and excellent dispersity in aqueous solution. Moreover, NIR absorption (690 nm) and bright fluorescence (800 nm) of CyN-12@NHs with a large Stokes shift (110 nm) in aqueous system make it an amenable high quality bioimaging contrast agent. The core-shell nanostructure significantly enhances the chemical and photo-stability of CyN-12 via the encapsulation, which possesses a 50-times longer half-life period than free CyN-12, along with a better resistance to reactive oxygen species ((ROS). Furthermore, in living cell imaging, CyN-12@NHs shows nearly no cytotoxicity and is able to outline the HepG2 cells. The in vivo imaging on a tumor-bearing mouse model indicates that CyN-12@NHs selectively accumulates in the liver after intravenous injection, and has a long retention in tumor after intra-tumor injection without decrease in fluorescence activity. Overall, the excellent photo-properties of CyN-12@NHs could meet the intricate requirements for tumor imaging, such as high sensitivity, sufficient tissue penetration, and high spatial resolution. The strategy of the silica-cyanine hybrid nanoparticles paves a desirable and efficient route to fabricate highly hydrophilic NIR fluorescent contrast agents for tumor imaging and therapy, especially with a breakthrough in photo-stability, bright fluorescences as well as large Stokes shit.

- Decoration of Gold Nanoparticles by a Double-Armed Calix[4]pyrrole: A Receptor-Decorated Nanoensemble for Anion Sensing and Extraction.

Sokkalingam, P.; Hong, S.-J.; Aydogan, A.; Sessler, J. L.; Lee, C.-H. *Chem. Eur. J.* **2013**, *19*, 5860–5867.

Abstract:



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Decoration of Gold Nanoparticles by a Double-Armed Calix[4]pyrrole: A Receptor-Decorated Nanoensemble for Anion Sensing and Extraction

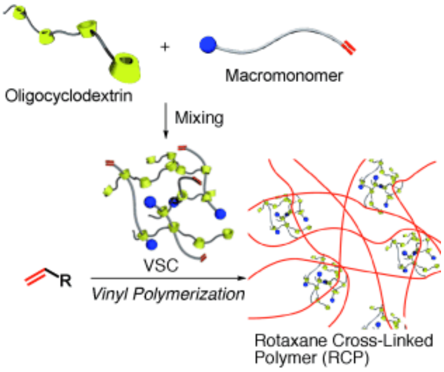
Punidha Sokkalingam,[a] Seong-Jin Hong,[a] Abdullah Aydogan,[b] Jonathan L. Sessler,*[b] and Chang-Hee Lee*[a]

Gold nanoparticles decorated with a double-armed, deep-cavity calix[4]pyrrole were prepared and fully characterized. Transmission electron microscopy imaging revealed that the average diameter of the particles was approximately 4 nm both before and after attachment of the receptor to the surface. The calix[4]pyrrole-functionalized nanoparticles exhibited highly elevated sensing behavior (approximately 1000 times in dichloromethane) relative to its monomeric congener while maintaining its guest selectivity. The receptor–nanoparticle conjugate (nanoreceptor) showed significant aggregation upon addition of the biphenolate anion, an effect ascribed to anion-mediated interparticle linking. The receptor–nanoparticle conjugate is also capable of extracting the fluoride anion (as its tetrabutylammonium salt) from an aqueous layer to an organic medium. Control experiments revealed that this extraction is not possible when using the analogous monomeric receptor.

- Versatile Supramolecular Cross-Linker: A Rotaxane Cross-Linker That Directly Endows Vinyl Polymers with Movable Cross-Links

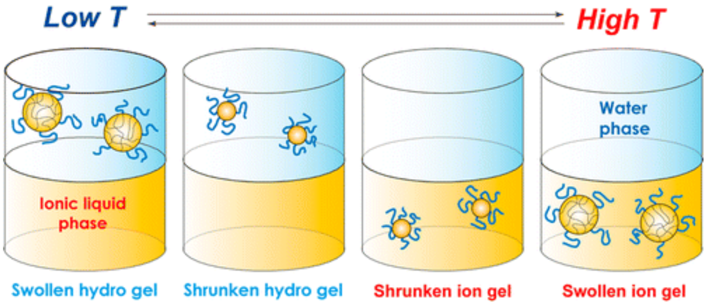
  Arai, T. ; Jang, K. ; Koyama, Y. ; Asai, S. ; Takata, T. *Chem. Eur. J.* **2013**, *19*, 5917–5923.

  Abstract:



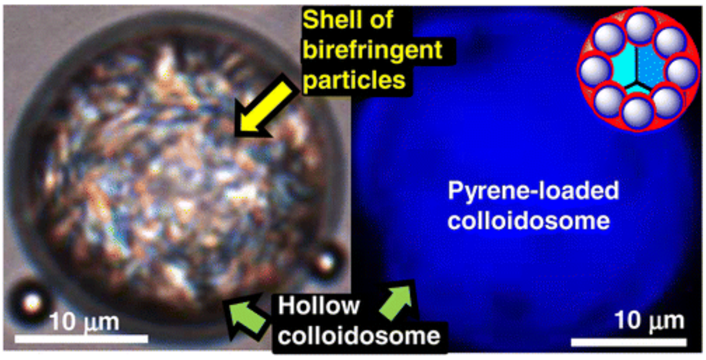
A supramolecular cross-linked cross-linker, capable of introducing rotaxane cross-links to vinyl polymers, has been developed for the rational synthesis of polyrotaxane networks. The experimental results reveal that the combination of an oligocyclodextrin (OCD) and a terminal bulky group-tethering macromonomer (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, $\mathrm{RCP_{DMAAm}}$, 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.

- Thermoreversible Nanogel Shuttle between Ionic Liquid and Aqueous Phases
  Ueki, T.; Sawamura, S.; Nakamura, Y.; Kitazawa, Y. ; Kokubo, H.; Watanabe, M. *Langmuir* **2013**, *45*, 13661–13665.
  Abstract:



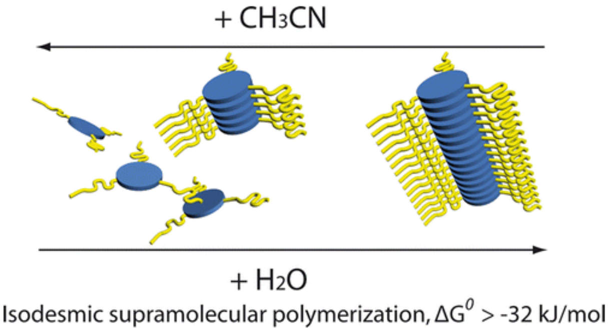
We describe a nanogel that can reversibly shuttle between a hydrophobic ionic liquid (IL) phase and an aqueous phase in response to temperature changes. A thermosensitive diblock copolymer, consisting of poly(ethylene oxide) (PEO) as the first segment and a random copolymer of *N*-isopropylacrylamide (NIPAm) and *N*-acryloyloxysuccinimide (NAS) as the second segment, was prepared as a nanogel precursor using anionic ring-opening polymerization of EO followed by reversible addition–fragmentation chain-transfer (RAFT) polymerization of NIPAm and NAS. After the micellization of the diblock copolymer in an aqueous solution upon heating to temperatures higher than the lower critical solution temperature (LCST) of the second segment, a coupling reaction of the NAS group of the P(NIPAm-*r*-NAS) core with ethylenediamine gave a nanogel with a well-solvated PEO corona. The nanogel exhibited contrasting thermosensitivities in the aqueous and IL phases. Dynamic light scattering measurements revealed that the nanogel exhibited LCST phase behavior (low-temperature-swollen/high-temperature-shrunken) in the aqueous phase and the opposite upper critical solution temperature (UCST) phase behavior (high-temperature-swollen/low-temperature-shrunken) in hydrophobic ILs. The nanogel favored the aqueous phase at low temperatures and the IL phase at high temperatures because of the solubility changes in the PEO corona. Upon increasing the temperature, the nanogel underwent a swollen-to-shrunken phase change in the aqueous phase, a transfer from the aqueous phase to the IL phase, and a shrunken-to-swollen phase change in the IL phase. These processes were thermally reversible, which made the round-trip shuttling of the nanogel between the aqueous and IL phases possible.

- Hollow Colloidosomes Prepared Using Accelerated Solvent Evaporation
  Shahidan, N. N.; Liu, R.; Thaiboonrod, S.; Alexander, C.; Shakesheff, K. M., Saunders, B. *Langmuir* **2013**, *45*, 13676–13685.
  Abstract:



We demonstrate a new, scalable, simple, and generally applicable two-step method to prepare hollow colloidosomes. First, a high volume fraction oil-in-water emulsion was prepared. The oil phase consisted of CH_2Cl_2 containing a hydrophobic structural polymer, such as polycaprolactone (PCL) or polystyrene (PS), which was fed into the water phase. The water phase contained poly(vinylalcohol), poly(*N*-isopropylacrylamide), or a range of cationic graft copolymer surfactants. The emulsion was rotary evaporated to rapidly remove CH_2Cl_2. This caused precipitation of PCL or PS particles which became kinetically trapped at the periphery of the droplets and formed the shell of the hollow colloidosomes. Interestingly, the PCL colloidosomes were birefringent. The colloidosome yield increased and the polydispersity decreased when the preparation scale was increased. One example colloidosome system consisted of hollow PCL colloidosomes stabilized by PVA. This system should have potential biomaterial applications due to the known biocompatibility of PCL and PVA.

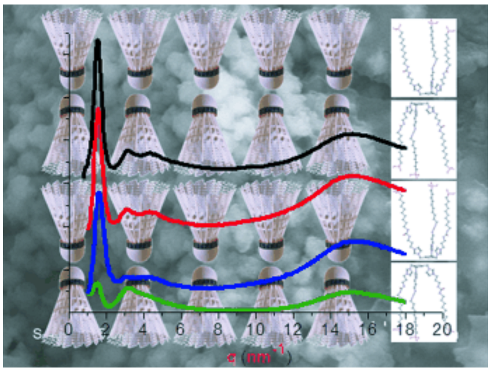
- Solvent-Dependent Disassembly of Amphiphilic OPE-Based Tricarboxamides
  Buendía, J.; Sánchez, L. *Org. Lett.* **2013,** *15*, 5746-5749.
  Abstract:



A series of water-compatible C_3-symmetric tricarboxamides endowed with a large number of EO side chains separated from the amide groups by different paraffinic linkers has been synthesized. The addition of a small amount of water breaks the N–H···O═C amide H-bonds but induces the formation of aggregates by a solvophobic effect. The lack of highly directional H-bonding interactions results in an isodesmic supramolecular polymerization with a calculated Gibbs free energy of −31.26 and −36.79 kJ mol^{-1} for **1** and **3**, respectively.

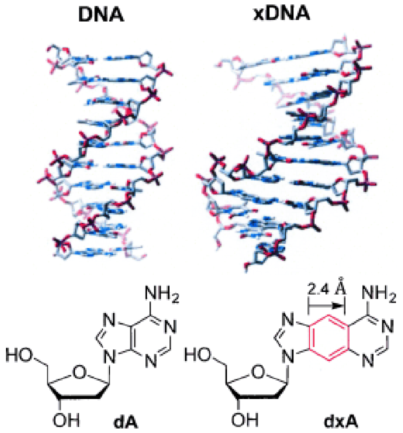
- Nanostructuring of Ionic Bridged Silsesquioxanes
  Monge-Marcet, A.; Cattoën, X.; Dieudonné, P.; Pleixats, R.; Man, M. W. C. *Chem. Asian J.* **2013**, *8*,

2235–2241.
Abstract:



The transformation by hydrolysis/condensation of four new mesityl-(bis or tris)imidazolium-based alkoxysilane precursors into their corresponding bridged silsesquioxanes has been investigated. These precursors feature urea groups and either short or long alkylene chains, which are known to favor self-assembly. The most regular nanostructures were obtained by a combination of the tripodal precursors with $C_{10}H_{20}$ alkylene chains, as shown by powder X-ray diffraction (PXRD) analysis, independent of the reaction conditions.

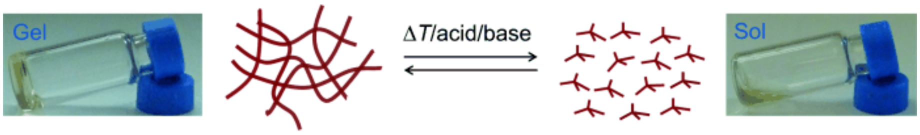
- Artificial Genetic Sets Composed of Size-Expanded Base Pairs
  Winnacker, M.; Kool, E. T. *Angew. Chem. Int. Ed.* **2013**, *52*, 12498–12508.
  Abstract:



We describe in this Minireview the synthesis, properties, and applications of artificial genetic sets built from base pairs that are larger than the natural Watson–Crick architecture. Such designed systems are being explored by several research groups to investigate basic chemical questions regarding the functions of the genetic information storage systems and thus of the origin and evolution of life. For example, is the terrestrial DNA structure the only viable one, or can other architectures function as well? Working outside the constraints of purine–pyrimidine geometry provides more chemical flexibility in design, and the added size confers useful properties such as high binding affinity and helix stability as well as fluorescence. These features are useful for the investigation of fundamental biochemical questions as well as in the development of new biotechnological, biomedical, and nanostructural tools and methods.

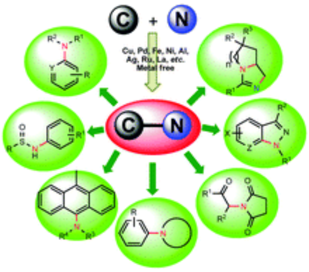
- A Supramolecular Gel from a Quadruple Zwitterion that Responds to Both Acid and Base
  Hisamatsu, Y.; Banerjee, S.; Avinash, M. B.; Govindaraju, T.; Schmuck, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 12550–12554.

Abstract:



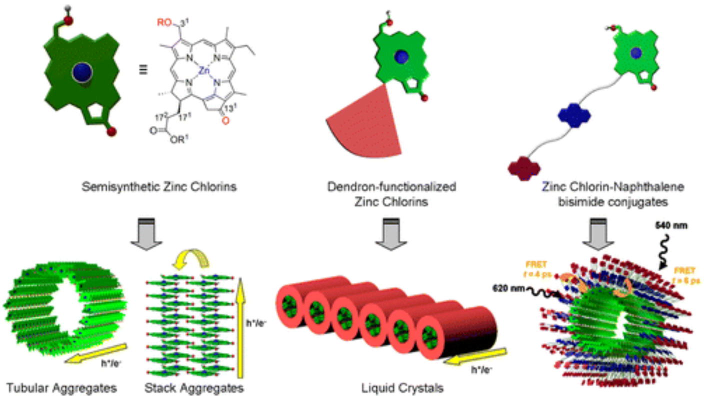
Four arms: A quadruple zwitterion based on a pentaerythritol core forms thermoreversible gels in DMSO driven by the formation of ion-paired dimers between the zwitterionic units. Furthermore, it exhibits reversible gel–sol transitions in response to both acid and base.

- C–N bond forming cross-coupling reactions: an overview
  Bariwal, J.; Van der Eycken, E. *Chem. Soc. Rev.* **2013**, *42*, 9283-9303.
  Abstract:



Nitrogen containing compounds are of great importance because of their interesting and diverse biological activities. The construction of the C–N bond is of significant importance as it opens avenues for the introduction of nitrogen in organic molecules. Despite significant advancements in this field, the construction of the C–N bond is still a major challenge for organic chemists, due to the involvement of harsh reaction conditions or the use of expensive catalysts in many cases. Thus, it is a challenge to develop alternative, milder and cheaper methodologies for the construction of C–N bonds. Herein, we have selected some prime literature reports that may serve this purpose.

- Chlorophyll J-Aggregates: From Bioinspired Dye Stacks to Nanotubes, Liquid Crystals, and Biosupramolecular Electronics
  Sengupta, S.; Würthner, F.; *Acc. Chem. Res.* **2013**, *46*, 2498–2512.
  Abstract:

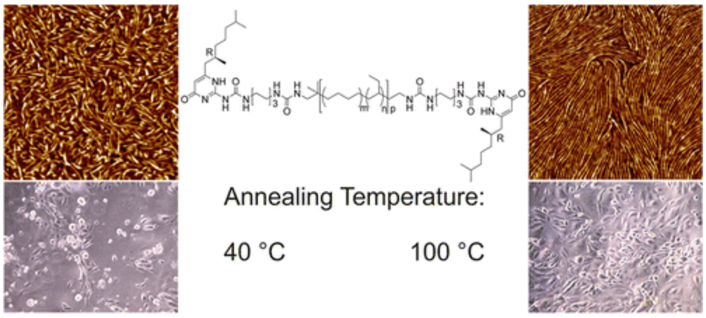


Among the natural light-harvesting (LH) systems, those of green sulfur and nonsulfur photosynthetic bacteria are exceptional because they lack the support of a protein matrix. Instead, these so-called chlorosomes are based solely on “pigments”. These are self-assembled bacteriochlorophyll *c*, *d*, and *e* derivatives, which consist of a chlorophyll skeleton bearing a 3^1-hydroxy functional group. Chemists consider the latter as an essential structural unit to direct the formation of light-harvesting

self-assembled dye aggregates with J-type excitonic coupling. The intriguing properties of chlorosomal J-type aggregates, particularly narrow red-shifted absorption bands, compared with monomers and their ability to delocalize and migrate excitons, have inspired intense research activities toward synthetic analogues in this field. The ultimate goal of this research field is the development of (opto-)electronic devices based on the architectural principle of chlorosomal LH systems. In this regard, the challenge is to develop small, functional building blocks with appropriate substituents that are preprogrammed to self-assemble across different length scales and to emulate functions of natural LH systems or to realize entirely new functions beyond those found in nature. In this Account, we highlight our achievements in the past decade with semisynthetic zinc chlorins (ZnChls) as model compounds of bacteriochlorophylls obtained from the naturally most abundant chlorin precursor: chlorophyll *a*.

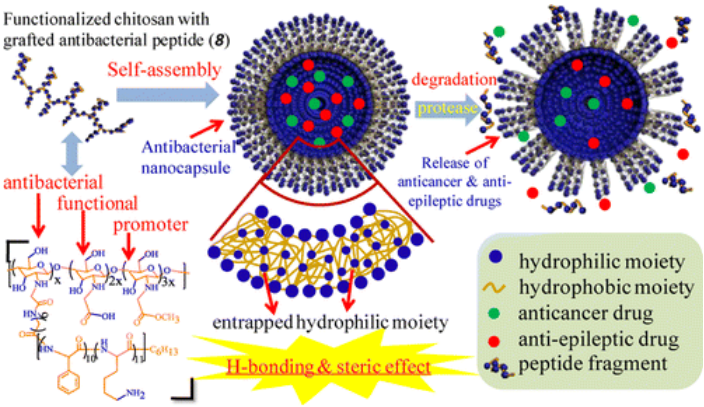
To begin, we explore how supramolecular strategies involving π-stacking, hydrogen bonding, and metal–oxygen coordination can be used to design ZnChl-based molecular stack, tube, and liquid crystalline assemblies conducive to charge and energy transport. Our design principle is based on the bioinspired functionalization of the 3^1-position of ZnChl with a hydroxy or methoxy group; the former gives rise to tubular assemblies, whereas the latter induces stack assemblies. Functionalization of the 17^2-position with esterified hydrophilic or hydrophobic chains, dendron-wedge substituents, and chromophores having complementary optical properties such as naphthalene bisimides (NBIs) is used to modulate the self-assembly of ZnChl dyes. The resulting assemblies exhibit enhanced charge transport and energy transfer abilities. We have used UV/vis, circular dichroism (CD), fluorescence spectroscopy, and dynamic light scattering (DLS) for the characterization of these assemblies in solution. In addition, we have studied assembly morphologies by atomic force microscopy (AFM), scanning tunneling microscopy (STM), transmission electron microscopy (TEM), and cryogenic-TEM. Crystallographic techniques such as powder X-ray and solid-state NMR have been used to explain the precise long- and short-range packing of dyes in these assemblies. Finally, functional properties such as charge and energy transport have been explored by pulse radiolysis time-resolved microwave conductivity (PR-TRMC), conductive AFM, and time-resolved fluorescence spectroscopy. The design principles discussed in this Account are important steps toward the utilization of these materials in biosupramolecular electronics and photonics in the future.

- From Molecular Structure to Macromolecular Organization: Keys to Design Supramolecular Biomaterials
  Hutin, M.; Burakowska-Meise, E.; Appel, W. P. J.; Dankers, P. Y. W.; Meijer, E. W. *Macromolecules* **2013**, *46*, 8528–8537.
  <u>Abstract:</u>



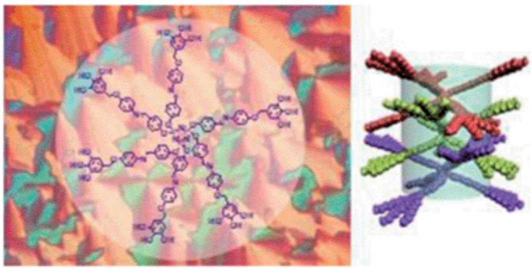
In the past decade, significant progress has been made in the field of biomaterials, for potential applications in tissue engineering or drug delivery. We have recently developed a new class of thermoplastic elastomers, based on ureidopyrimidinone (UPy) quadruple hydrogen bonding motifs. These supramolecular polymers form nanofiber-like aggregates initially via the dimerization of the UPy units followed by lateral urea-hydrogen bonding. Combined kinetic and thermodynamic studies unravel the pathway complexity in the formation of these polymorphic nanofibers and the subtlety of the polymer's design, while these morphologies are so critically important when these materials are used in combination with cells. We also show that the cell behavior directly depends on the length and shape of the nanofibers, illustrating the key importance of macromolecular and supramolecular organization of biomaterials. This study leads to new design rules that determine what factors are decisive for a polymer to be a good candidate as biomaterial.

- Antibacterial Polypeptide-Grafted Chitosan-Based Nanocapsules As an “Armed” Carrier of Anticancer and Antiepileptic Drugs
  Zhou, C.; Wang, M.; Zou, K.; Chen, J.; Zhu, Y.; Du, J. *ACS Macro Lett.* **2013**, *2*, 1021–1025.
  Abstract:



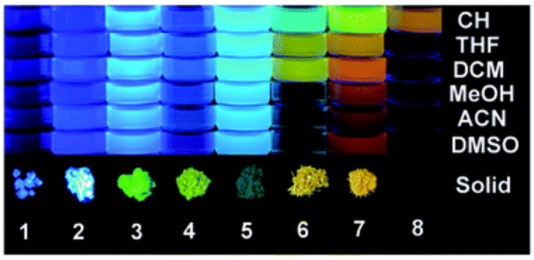
Antibacterial polypeptides as ancient immune defense systems are effective against bacteria. Here we report a novel kind of “armed” carrier: an antibacterial polypeptide-grafted chitosan-based nanocapsule with an excellent antibacterial efficacy against both Gram-positive and Gram-negative bacteria. This nanocapsule also has excellent blood compatibility and low cytotoxicity. Patients after tumor surgery may benefit from this “armed” carrier because it is highly anti-inflammation and is able to deliver anticancer and antiepileptic drugs simultaneously.

- Synthesis and characterization of room temperature columnar mesogens of cyclotriphosphazene with Schiff base units
  He, Q.; Dai, H.; Tan, X.; Cheng, X.; Liu, F.; Tschierskec, C. *J. Mater. Chem. C* **2013***, 1,* 7148–7154.
  Abstract:



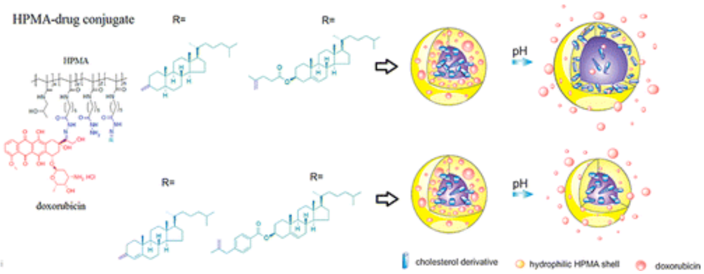
New supermolecular liquid crystals have been synthesized by attaching polycatenar aromatic units with three terminal alkyl chains through imine linking groups to a central cyclotriphosphazene ring, and these were investigated by polarizing microscopy, DSC and XRD. Compounds with several different linear terminal alkyl chains can form liquid crystals with columnar phases, and most of these are room temperature columnar phases. A model is proposed for the organization of the molecules in the columns, which is based on the nanosegregation of the aromatic cores and alkyl chains and a staggered organization of the star-shaped molecules in columns. Branching of the peripheral alkyl chains leads to an amorphous material.

- Full-colour luminescent compounds based on anthracene and 2,2′-dipyridylamine
  Chen, B.; Yu, G.; Li, X.; Ding, Y.; Wang, C.; Liu, Z.; Xie, Y. *J. Mater. Chem. C* **2013**, *1,* 7409–7417.
  Abstract:



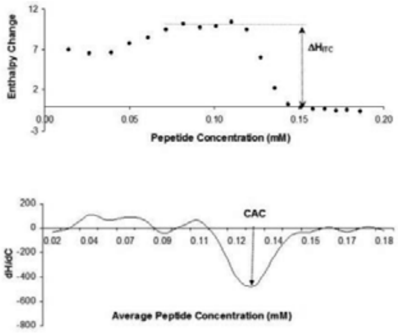
Starting from two simple units of anthracene and 2,2′-dipyridylamine, a series of new luminescent compounds 1–8 were designed and synthesized by a combined strategy of changing the connection mode between the two units, extending the conjugation size, and introducing an additional electron donor. Photophysical properties of 1–8 were investigated and discussed on the basis of solvatochromic behaviour, theoretical calculations, crystal structure, and optimized structures. Interestingly, the emission wavelengths of these compounds could be successfully tuned from violet to red both in solutions and the solid-state, and prominent positive solvatochromism was observed for the compounds with a D–π–A framework. Consider compound 7 as an example, it shows peaks at 526 nm and 627 nm in cyclohexane and DMSO, respectively. Meanwhile, the quantum yield was decreased from 0.80 in cyclohexane to 0.12 in DMSO. The introduction of bulky groups was demonstrated to be effective for suppressing the aggregation effect and thus improving the solid state emission quantum yield. These results indicate that the combined structure modulation strategy offers a powerful tool for tuning the emission behaviour. To demonstrate the possibility of practical applications, 2 was employed as the emitting material for the fabrication of deep-blue organic light-emitting diodes (OLEDs), which showed a maximum external quantum efficiency of 2.2%. The CIE coordinates of (0.15, 0.08) are indicative of excellent blue color purity.

- Hydrolytically Degradable Polymer Micelles for Drug Delivery: A SAXS/SANS Kinetic Study
  Filippov, S. K.; Franklin, J. M.; Konarev, P. V.; Chytil, P.; Etrych, T.; Bogomolova, A.; Dyakonova, M.; Papadakis, C. M.; Radulescu, A.; Ulbrich, K.; Stepanek, P.; Svergun, D. I. *Biomacromolecules* **2013**, *14*, 4061–4070.
  Abstract:



We report kinetic studies of therapeutically highly potent polymer–drug conjugates consisting of amphiphilic *N*-(2-hydroxypropyl) methacrylamide (HPMA)-based copolymers bearing the anticancer drug doxorubicin (Dox). Highly hydrophobic cholesterol moieties as well as the drug were attached to the polymer backbone by a pH-sensitive hydrazone bond. Moreover, the structure of the spacer between the polymer carrier and the cholesterol moiety differed in order to influence the release rate of the hydrophobic moiety, and thus the disintegration of the high-molecular-weight micellar nanoparticle structure. We performed time-dependent SAXS/SANS measurements after changing pH from a typical blood value (pH 7.2) to that of tumor cells (pH 5.0) to characterize the drug release and changes in particle size and shape. Nanoparticles composed of the conjugates containing Dox were generally larger than the drug-free ones. For most conjugates, nanoparticle growth or decay was observed in the time range of several hours. It was established that the growth/decay rate and the steady-state size of nanoparticles depend on the spacer structure. From analytical fitting, we conclude that the most probable structure of the nanoparticles was a core–shell or a core with attached Gaussian chains. We concluded that the spacer structure determined the fate of a cholesterol derivative after the pH jump. Fitting results for 5α-cholestan-3-onecholestan-3-one and cholesteryl-4-oxopentanoate (Lev-chol) implied that cholesterol moieties continuously escape from the core of the nanoparticle core and concentrate in the hydrophilic shell. In contrast, cholest-4-en-3-one spacer prevent cholesterol escaping. Dox moiety release was only observed after a change in pH. Such findings justify the model proposed in our previous paper. Lastly, the cholesteryl 4-(2-oxopropyl)benzoate (Opb-Chol) was a different case where after the release of hydrophobic Opb-Chol moieties, the core becomes more compact. The physicochemical mechanisms responsible for the scenarios of the different spacers are discussed.

- Toward a Mechanistic Understanding of Ionic Self-Complementary Peptide Self-Assembly: Role of Water Molecules and Ions
  Kabiri, M.; Bushnak, I.; McDermot, M. T.; Unsworth, L. D. *Biomacromolecules* **2013**, *14*, 3943–3950.
  Abstract:



Ionic self-complementary peptides are considered an important class of self-assembling peptides. In particular, RADARADARADARADA ($RADA_4$) is well-known to form a relatively regular nanofiber structure that has been primarily studied in terms of its physicochemical properties, as related to its biomedical applications. However, the molecular level interactions that are involved in promoting the self-assembly of this peptide into nanofibers have not been fully elucidated. Herein, a thermodynamic analysis of the influences of peptide chemistry upon self-assembly is discussed for $RADA_4$, $RADA_4$-K_5, and $RADA_4$-S_5. The regular nanofiber structure of the assembled peptides makes it a good candidate for isothermal titration calorimetry (ITC) studies for determining the propensity for self-assembly, the critical assembly concentration (CAC), and the role hydration and ion content play in the assembly of these peptides. First, solutions containing only $RADA_4$-K_5 did not self-assemble; illustrating even slight alterations in the asymmetric terminal amino acid chemistry affects assembly. The CAC of the remaining self-assembling peptides was between ~0.1 and ~0.15 mM. Interestingly, we found that self-assembly was entropically driven with hydrophobic forces being the main driving force for $RADA_4$ and hydrogen bonding for $RADA_4$-S_5. The role of water molecules and counterions in self-assembly was also highlighted: assembly of $RADA_4$ led to desolvation of interfacial surfaces, whereas the net number of water molecules in the assembled complex increased upon $RADA_4$-S_5 self-assembly. Moreover, it was found that counterions did not seem to contribute significantly to self-assembly: a result in contrast to current concepts regarding the role of electrostatic interactions in self-assembly of $RADA_4$-like peptides. A molecular level understanding of peptide self-assembly will allow for further engineering of peptides for a vast array of biomedical applications.