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Cucurbituril-based supramolecularly engineered nanostructured materials

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Abstract

Cucurbituril (CB) is a unique macrocycle with a rigid symmetrical structure which is composed of two identical hydrophilic portals decorated with partially negatively charged carbonyl groups and a hydrophobic cavity. A number of different nanostructured materials including nanoparticles, nanocomposites, vesicles, rods and so forth have been prepared by taking advantage of the varying cavity size of the CB homologues, their ability to accommodate more than one guests in their cavities, their rigid symmetrical structures as well as the water solubility of CB7. These nanostructures could find a wide range of potential applications in the areas of self-healing materials, nanomedicine, plasmonics, and nanocatalysis. Here, we review the recent progresses in the synthesis, properties and application of CB-based supramolecularly engineered nanostructures which are either constructed through CB-assisted self-assembly or from the post functionalized CB homologous.

1. Introduction

The products of acid-catalyzed condensation of glycoluril with formaldehyde were first reported as a white amorphous material by Behrend *et al.* in 1905.[1] In 1981 Mock and co-workers revisited the work of Behrend and determined the structure of this material as a macrocyle containing six units of glycoluril.[2] Nowadays it is known as cucurbit[6]uril (CB6), where 6 represents the number of glycoluril units in the macrocycle. In 1990s Kim and co-workers have started to report a series of very elegant works on CB6 contributing substantially to the field of CB.[3-5] In 2000 three new CB homologues, CB5, CB7 and CB8 having 5, 7 and 8 glycoluril units respectively, have been discovered.[6, 7] Especially the discovery of CB7 has excited the supramolecular chemistry community because of its both large cavity and water solubility which are very important features for biological applications.[8-11] In 2002 Day and co-workers reported CB10 interlocked with CB5.[12] The very fast development of cucurbituril field leads to the preparation of a number of different

CB homologues and derivatives in recent years. For example the inverted CB6 and inverted CB7,[13] the chiral nor-seco-cucurbituril (±)-bis-ns-CB6 and the nor-seco-CB10,[14] were all reported. Recently, also the synthesis of large CB derivatives as hemi-CB12[15] and twisted CB14[16] were described.

CBs have two hydrophilic portals decorated with partially negatively charged carbonyl groups and a hydrophobic cavity. Owing to these features they serve as an excellent host for hydrophobic molecules. Host-guest interaction of CBs is based on two main intermolecular forces: hydrophobic effect and ion dipole interactions at the carbonyl portals. Higher binding affinity comparing to the same class of macrocycles (cyclodextrins, calixarenes) is attributable to their shape (narrow portals and wider hydrophobic cavity) and carbonyl groups which provides selective binding through positively charged guest molecules. Mock and co-workers extensively studied on selectivity, recognition and self-sorting properties of CB6.[17,18] However, CB-relating studies exponentially increased by the isolation and characterization of CB7 and CB8 having larger cavities than CB6 and moreover due to water-solubility of CB7. Thus, selectivity, high binding affinity, recognition properties and the water-solubility of some CB homologous allow the use of CB family in biological, photochemical, electrochemical, catalytic and optoelectronic applications. CBs are also very useful building blocks in the preparation of nanomaterials. There are numerous studies on the host-guest chemistry of CB homologous and their recognition properties as well as a number of nice review papers outlining the synthesis, properties and applications of CB homologous.[19-24]

In this review, we will be mainly focusing on the synthesis, properties and application of CB-based nanostructures which are either constructed through CB-assisted self-assembly or from the post functionalized CB homologous. We are also going to discuss briefly the synthetic routes used in the CB-functionalization.

2. Synthesis of nanostructures assembled through CB-assisted self-assembly

A number of different nanostructures have been constructed by taking advantage of the interesting features of CBs. The characteristic of two identical portals decorated with partially negatively charged carbonyl groups and their rigid symmetrical structures were taken as an advantage in the preparation of metal nanoparticles; CBs acted as a capping agent to stabilize the gold or silver nanoparticles in the aqueous solutions. Moreover, CB-capped gold nanoparticles have been nicely utilized in the surface enhanced Raman scattering spectroscopy and plasmonics as well as in the catalysis.

Varying cavity size of the CB homologues and the ability of accommodating more than one guests in their cavity, rigid symmetrical structure and water solubility of some of its homologues allowed the preparation of nanoparticles, nanocomposites, vesicles, rods and etc. In the following section we are going to review the recent works relating to CB-containing metal nanoparticles and CB-assisted self-assembled nanostructures through host-guest chemistry.

2.1 Supramolecular assemblies of cucurbituril with metal nanoparticles

Here we are going to discuss mainly the following points: CB's role as a capping agent to stabilize metal nanoparticles such as gold and silver, CB-containing hybrid nanostructures made out of appropriately functionalized polymeric nanoparticles and metal nanoparticles as well as the function of CB in the formation of plasmonic nanostructures. These nanostructures could find applications in the area of sensing, optoelectronic device fabrication, surface functionalized assemblies and catalysis.

2.1.1 Synthesis of CB-containing gold and silver nanoparticles

Water-dispersible gold and silver nanoparticles have many potential applications including catalysis, chemo and biosensors, biomedical applications as well as plasmonics.

To utilize these nanoparticles for catalytic applications, preferably capping agents stabilizing the nanoparticles should not strongly bind to the surface of the metal nanoparticles. To this end, CBs have been found to be suitable for this purpose.

One of the first works regarding CB-containing gold nanoparticles was conducted by Corma and co-workers. They claimed the formation of gold clusters inside the cavity of CB but this study was not furthered.[25] Geckeler et al reported the synthesis of water dispersible gold nanoparticles in the presence of CB7 without using any reducing agent.[26] They concluded that CB is acting as a capping agent to stabilize the gold nanoparticles as well as a reducing agent.

They have also demonstrated the use of these nanoparticles as a catalyst in the reduction of nitrophenol in the presence of sodium borohydride. They explained the catalytic ability of these nanoparticles with the loose attachment of CBs through carbonyl portals to the gold surfaces making room for substrates which will interact with the surface in order to be catalysed.

Sherman et al contributed substantially for the development of this field by conducting detailed works. In one of the early works, they prepared CB5-capped gold nanoparticles by reducing $HAuCl_4$ with $NaBH_4$ in the presence of various amounts of CB5 (Fig.1).[27] They

observed the formation of dynamic aggregates consisting of a controllable ratio of singly and doubly capped CB5.

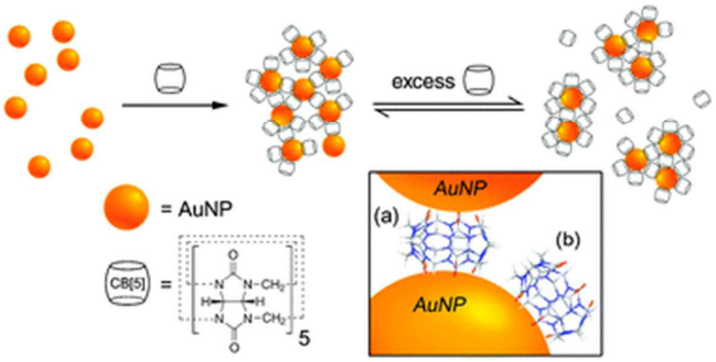


Fig. 1 The preparation of CB5-capped gold nanoparticles and the formation of dynamic aggregates consisting of a controllable ratio of singly and doubly capped CB5. (Reprinted with permission from ref. 27. Copyright 2010 Royal Society of Chemistry.)

The same group went on and conducted a detailed systematic work on supramolecular capping of CB homologues (CB5-CB8).[28] First metastable gold nanoparticles were prepared by reducing $HAuCl_4$ with $NaBH_4$ and then CB solutions were added to these metastable gold nanoparticle aqueous dispersions to stabilize further the gold nanoparticles by capping with CB homologues. These CB-capped nanoparticles were stable in solution, and were found to form reversible aggregates based on singly and doubly capped CBs. The system was further stabilized by the complexation of sodium cations with the vacant carbonyl portals of the singly capped CBn molecules.

Although ligandless, CB-capped silver nanoparticles could find potentially many interesting applications, they have not been as widely studied as gold nanoparticles. Masson et al. studied the formation and stabilization of silver nanoparticles with CB5, CB6, CB7 and CB8 as well as cucurbituril-based pseudorotaxanes in aqueous medium.[29] In this work nanoparticles of silver-CB were prepared by reducing $AgNO_3$ with $NaBH_4$ in the presence of CB homologues. CB homologues caused different effects on the silver nanoparticles. While CB7 and CB8 allow the formation of stable solutions of narrowly dispersed nanoparticles with the size of 5.3 and 3.7 nm, respectively, CB5 and CB6 induced rapid aggregation and sedimentation. The authors attributed the instability of Ag nanoparticles and the aggregate formation in the presence of CB5 and CB6 due to the rigidity of CB5 and CB6 and as a result their possible lack of suitable arrangement at the silver surface. However, having stable CB-

capped Ag nanoparticle aqueous dispersion in the case of CB7 and CB8 could be due to more flexible nature of the CB7 and CB8. Thus, they could be distorted to interact with Ag nanoparticle surfaces for the requirement of the stabilization. They have also supported this assumption on interactions between the silver nanoparticles and carbonyl portals of CBs by computer modelling.

They found that large excesses of silver or CB7 could trigger aggregate formation and the optimal $AgNO_3$/CB7 ratio for the formation of stable nanoparticles should be kept as 1:1-2:1. Moreover, it was shown that even filling the cavity of CBs with a bulky and positively charged guest affects insignificantly the stability of Ag/CB7 nanoparticles. This is a very important feature because the availability of the cavity of CB7 could be beneficial in many applications such as sensing.

The synthesis of Janus nanoparticles composed of Ag and AgBr was also reported.[30] Janus nanoparticles are basically nanoparticles having two or more different regions on which materials with different chemical and physical properties co-exist.[31] These nanoparticles might find many interesting applications ranging from photonics to biomedical applications. Especially metal Janus nanoparticles could be utilized as photocatalysts. In this work, AgBr nanoparticles were prepared from the aqueous solution of $AgNO_3$ and NaBr via nanoprecipitation method and the resulting nanoparticles were capped with CB5 or CB7 to further stabilize the nanoparticles. When these nanoparticles are irradiated with an electron beam, Ag^{+1} could be reduced to Ag^0, in this way they managed to obtain patchy nanoparticles containing AgBr and Ag nanoparticles in which CBs could stabilize both surfaces. Most importantly, the degree of the transformation can be directly followed through a transmission electron microscope.

Very recently, the preparation of CB7-capped gold nanoparticles in the absence of metallic cations and organic ligands have been reported.[32] The nanoparticles were prepared by reducing $HAuCl_4$ with H_2O_2 and applying 532 nm-laser light (18–20 mJ per pulse) to ablate the AuNPs generated in situ. CB-capped nanoparticles were found to be stable for prolonged time without forming any aggregates. Moreover, these CB-capped nanoparticles showed an enhanced catalytic activity toward reduction of dissolved O_2 due to a cooperative effect between their components by fixing oxygen to the nanoparticle surface and increasing the local concentration of oxygen.

2.1.2 The use of CB-capped gold nanoparticles in the Surface enhanced Raman scattering

The surface enhanced Raman scattering (SERS) is an optical phenomenon arising from the conjugation of molecules with metal nanoparticles such as gold or silver which show surface plasmon resonance due to oscillations of free electrons.[33] The Raman signals are significantly increased in the regions between closely spaced nanoparticles which are called 'hot spots', and as a result even the signal of a single molecule can be detected. Owing to the high sensitivity, this technique is very attractive for chemical and biological sensing.[33]

However, to create proper hot spots are not a trivial task and many efforts have been devoted to obtain efficient and reproducible results. In order to create hot spots, metal nanoparticles should be induced to form defined aggregates. Scherman and co-workers demonstrated that aqueous dispersion of CB-capped gold nanoparticles could be used as a substrate for SERS.[34, 35] To this end, aggregation of gold nanoparticles with CB5 produced rigid, fixed and reproducible interparticle separation of 0.9 nm. They observed strong and reproducible SERS from the AuNP:CB5 aggregates. Here CB acted as a SERS reporter, where the exploited resonant plasmon modes can be tuned in spectral position and time through the concentration of CB5 and the NP diameter. They have also demonstrated a SERS based assay using the host-guest complexation ability of CB in which the analyte molecule was subjected to intense field enhancement on the plasmonic hot spot created by CB-junctions.

When gold nanoparticles were capped with CB8 which is a member of CB family with a large cavity, it was possible to create precise subnanometer junctions between gold nanoparticles while its cavity simultaneously traps small molecules allowing their reproducible SERS detection.[36] Inclusion complex formation of CB8 with guests could produce characteristic SERS signals and this, in turn, will be very useful for absolute quantification of a range of molecules down to 10^{-11} M levels (Fig. 2).

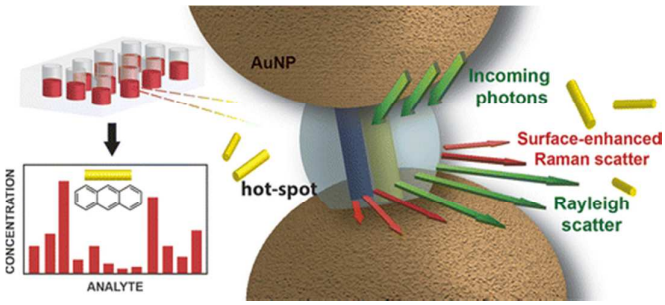


Fig. 2 Schematic of host−guest SERS analysis using ternary complexation: CB8 aggregates AuNPs and localizes the analyte in the hot-spot for SERS analysis. (Reprinted with permission from ref. 36. Copyright 2012 American Chemical Society.)

One-dimensional metal nanoparticle chains are very important in the area of plasmonics owing to their high symmetry and ability to propagate plasmonic effect and the energy transfer along the chain.[37] However, finding a precise junction between the nanoparticles to fabricate these nanostructures presents some challenges. Scherman and co-workers demonstrated the use of CB7 as nanojunctions of 0.9 nm in the electrokinetic assembly of one-dimensional nanoparticle chains (Fig.3).[38] A nanoporous polycarbonate membrane was used and the process was controlled by the applied voltage, the nanoparticle/CB7 concentration ratio, time and temperature. Extinction spectroscopy was used for the real-time analysis of the growth mechanism based on the chain plasmonics. It was also confirmed by TEM images that the chain length and linearity of the structures could be controlled by the tuning the parameters.

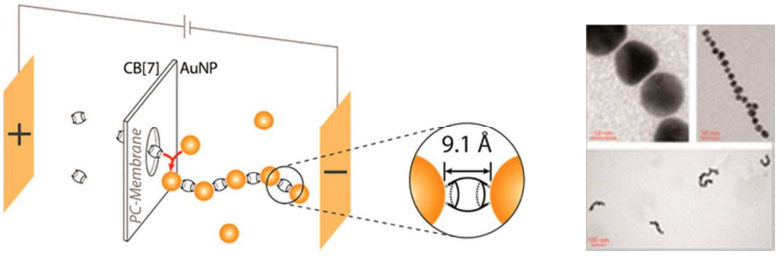


Fig. 3 The use of CB7 as nanojunctions of 0.9 nm in the electrokinetic assembly of one-dimensional nanoparticle chains. (Reprinted with permission from ref. 38. Copyright 2013 American Chemical Society.)

2.1.3 Supramolecular hybrid nanostructures

The formation of morphologically controlled, highly ordered arrays of nanoparticles is required in order to exploit the ability of metal nanoparticles in the device fabrication. For this endeavour, to form organic-inorganic composite materials many approaches have been adopted. Among them, the use of supramolecular approach can offer additional advantages such as controlled structures could be obtained and the system could be made reversible using especially host-guest approach.

Shermann and co-workers prepared gold nanoparticle-polymer nanocomposite by making use of the host guest chemistry of CB8.[39] It is well known that CB8 can accommodate more than one guests in its cavity and has high affinity toward some guests and it can form ternary complexes by simultaneously binding with electron rich and electron deficient guests such as a naphthol (Np) derivative and a methyl viologen dication (MV^{2+}), respectively. In

order to prepare nanoparticle-polymer composites, first MV^{2+} (guest 1) attached gold nanoparticles and poly(2-hydroxyethyl acrylamide)-co-(naphtholtriazole acrylamide) which contains the second guest of Np units (guest 2) were prepared (Fig. 4). Through ternary complex formation between CB8 and the guest one and two in water nanocomposite was obtained. In the absent of second guest and upon one electron reduction of viologen, 2:1 inclusion complexation between MV^{+} and CB8 took place which caused an interparticle aggregation in water and precipitation.

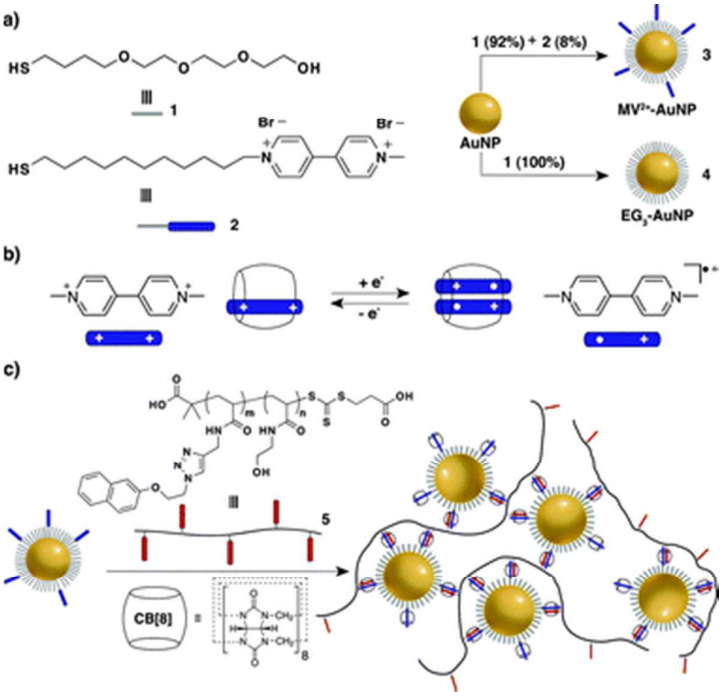


Fig. 4 The preparation of gold nanoparticle-polymer nanocomposite by making use of the host guest chemistry of CB8. (Reprinted with permission from ref. 39. Copyright 2011 Royal Society of Chemistry.)

The same approach in the preparation supramolecular gold-polymer composite material preparation was extended in the fabrication of mono disperse supramolecular microcapsules using microfluidic approach (Fig. 5).[40] Microdroplets by the narrow size distribution with a mean diameter of 59.6 mm were first generated in a microfluidic device, using a T-junction geometry. These microcapsules comprise of gold nanoparticles decorated with binding motifs MV^{2+} for CB8 and a polymer bearing a naphtol functionalities. Stable hollow microcapsules obtained upon dehydration can be loaded with a wide range of materials during capsule formation and the controlled release of the guest can be triggered through an external stimulus as a result of the supramolecular host-guest chemistry

incorporated in the capsule shell. Moreover, these microcapsules can be used as a SERS substrate due to their plasmonic properties inherited by the presence of gold nanoparticles in their structures.

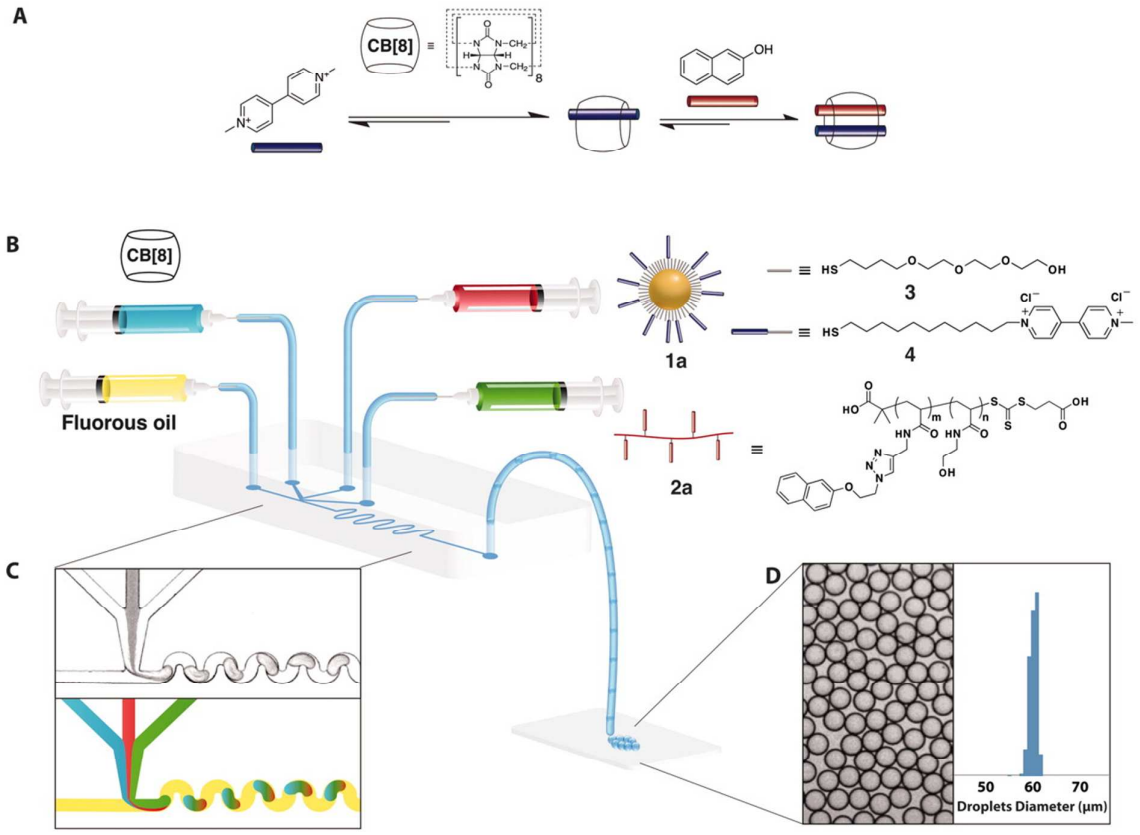


Fig. 5 The fabrication of mono disperse supramolecular microcapsules using microfluidic approach. (A) Schematic representation of a ternary complex formation between methyl viologen dication (MV^{2+}), 2-naphthol and CB8. (B, C, D) Microfluidic set-up for the preparation of hybrid-capsules. (Reprinted with permission from ref. 40. Copyright 2012 Science.)

Photoresponsive hybrid raspberry-like colloids (HRCs) were prepared employing the host-guest chemistry of CB8 (Fig. 6).[41] The core of the colloids consists of 4-hydroxyazobenzene- (Azo-) functionalized silica microspheres and the corona is based on methyl viologen (MV) decorated polymeric nanoparticles. HRCs were obtained by the formation of ternary complex between MV/trans-Azo and CB8 in water. The disassembly of

the system could be realized through the conformational changes of trans-azo to cis-azo moieties upon light irradiation.

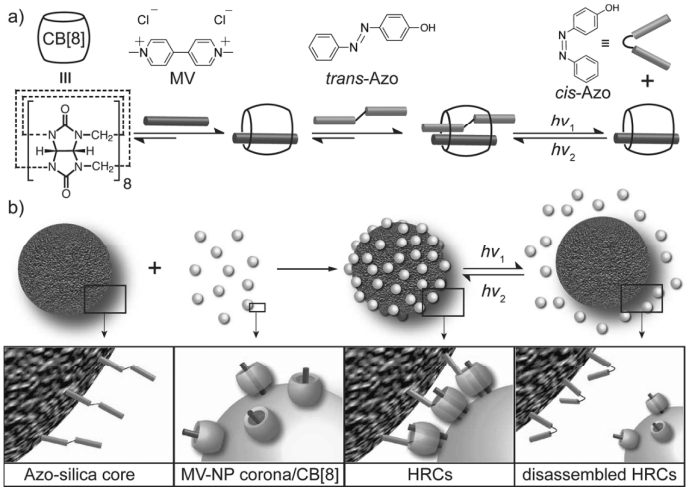


Fig. 6 (a) Ternary complex formation between MV, trans-azo and CB8 and the disassembly of ternary complex by a light stimulus; **(b)** Photoresponsive hybrid raspberry-like colloids (HRCs) prepared by the host-guest chemistry of CB8. (Reprinted with permission from ref. 41. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.)

Host-guest chemistry of CBs was also utilized in the preparation of therapeutic gold nanoparticles.[42] Gold nanoparticles decorated with diaminohexane groups exhibited initially high toxicity toward cells but the cytotoxicity of nanoparticles were reduced upon complexation of CB7 with diaminohexane groups by sequestering in endosomes. The toxicity of nanoparticles were reversed by administration of 1-adamantylamine (ADA) which has a higher affinity toward CB7 than 1,6-diaminohexane moieties and by complexing with CB7 leaving behind toxic AuNP–NH_2 to show their therapeutic effect toward cells (Fig. 7).[42]

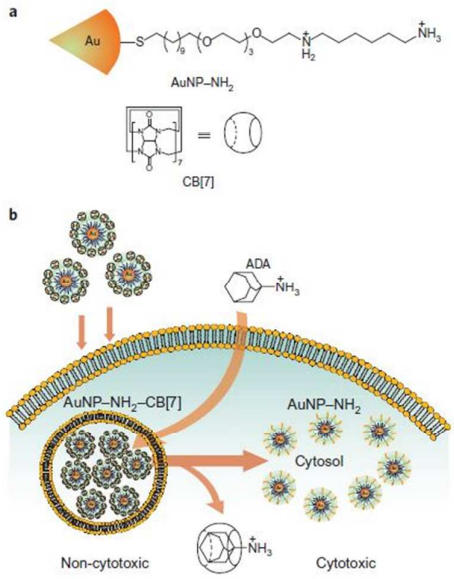


Fig. 7 Controlled release of gold nanoparticles triggered by 1-aminoadamantane. (Reprinted with permission from ref. 42. Copyright 2010 Nature Publishing Group.)

Similar approach was also used to regulate the toxicity of conjugated polymer nanoparticles[43] as well as to control the degree of protein-nanoparticle interaction by modulating the surface properties of NPs.[44]

Gold nanoparticles with different shapes can differ in their physical and chemical properties. Rod shaped-gold particles exhibit anisotropic optical and electronic responses which are very important features in plasmonics.[45] These nanostructures could also find applications in optical devices, biochemical sensors, and nanomedicine. For biomedical applications they should be water dispersible and their surfaces should be modified with biocompatible functionalities.

One of the examples of gold nanorods (GNRs) protected by a hydrophilic CB7-based pseudorotaxane anchored monolayer was reported by Li and co-workers.[46] 4,4'-bipyridinyl unit linked to an alkyl chain terminated with disulphide was first attached to gold nanorods and in water the threading of this axle by CB7 resulted in the formation of a pseudorotaxane. These structures were characterized by TEM, Raman spectroscopy, UV/Vis/NIR spectroscopy, and cyclic voltammetry (CV).

End-to-end assembly of Au nanorods can also be realized by host-guest chemistry of CBs with suitable functionalities attached on the end surfaces of the nanorods (Fig. 8). Viologen end-functionalised AuNRs were prepared with the use of cetyltrimethylammonium bromide (CTAB) as a stabilising ligand.[47] When the bifunctional linker containing the second

guest naphthyl moieties was introduced, through ternary complex formation between the end groups of AuNRs, linker and CB8, nanorods were assembled together to form oligomeric gold nanorod chains. Moreover, the length of the linker was found to be quite important; while a long and flexible linker causes aggregate formation, a short linker provides end-to-end connection. When CB7 was used instead of CB8 as a host, no chain formation was observed. Furthermore, the use of the competitive guest instead of linker produced no chain.

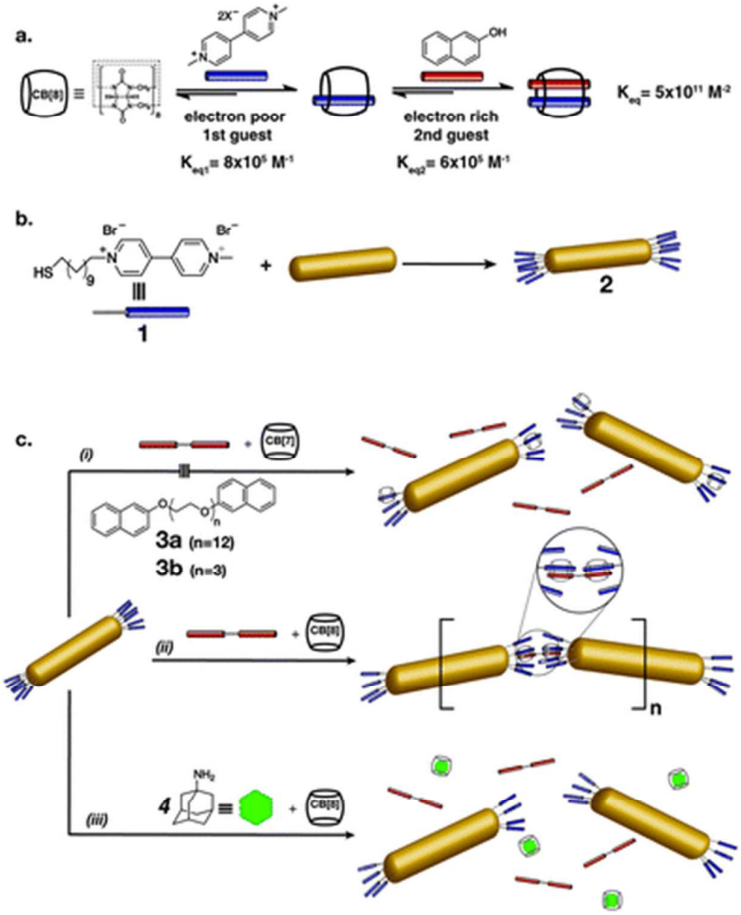


Fig. 8 (a) Formation of a ternary complex between methyl viologen, 2-napthol and CB8; (b) preparation of methyl viologen functionalized gold nanorods; (c) addition of either bi-naphthol linker with propyl or dodecyl spacers (i) with CB7, (ii) with CB8, or (iii) with CB8 in the presence of adamantylamine. (Reprinted with permission from ref. 47. Copyright 2013 Royal Society of Chemistry.)

In another study the contribution of CB in the design of a theranostic platform was demonstrated in such a way that CB7-functionalized iron oxide nanoparticles were prepared

for drug delivery and magnetic resonance imaging (MRI) by microwave heating.[48] The degree of CB7 attachment was monitored by several techniques including FT-IR spectroscopy, Zeta potential, dynamic light scattering measurements, high resolution transmission electron microscopy (HRTEM) and powder X-ray diffraction (PXRD). Density functional theory (DFT) calculations suggest the interaction of carbonyl oxygens of CB7 with surface Fe^{3+} ions. CB7-attached nanoparticles were found to be stable under a wide pH range (2–12) and have a transverse relaxivity, R2, of 113 s1 mM1. Nile red (NR) dye was loaded into the cavities of the surface-adsorbed CB7s, and intracellular delivery of the dye to HCT116 cells was observed by confocal laser scanning microscopy. The dye-loaded particles have a R2 of 172 s1 mM1.

2.2 CB-assisted formation of supramolecular nanostructures

By taking advantage of the rich host-guest chemistry of CB homologous, a number of different nanostructures have been prepared. Especially the ability of CB8 to form ternary complexes with electron rich (e.g. naphthol moity) and electron deficient (e.g. viologen cation) species has been extensively used in the construction of supramolecular nanostructures such as supramolecular hydrogel, nanoparticles, vesicles, supramolecular arrays and so forth. These nanostructures could find many interesting applications especially in the area of self-healing materials, the delivery of drug or other therapeutic materials and the area of theranostics as well as for controlling the viscosity of materials.

2.2.1 Supramolecular hydrogel

Hydrogels are basically three-dimensional hydrophilic polymeric networks which have high capacity to hold water.[49] Depending on the structure of polymer and the cross-linking density their swelling degree may vary. These materials resemble the biological tissues and as a result they are quite important for biomedical applications.[50]

Hydrogels can be prepared using a number of different methods including cross-linking of appropriate polymers through covalent bonds and non-covalent bonds (supramolecular approach). Supramolecular approach can offer reversibility to the structure and the resulting materials can be used for self-healing and tuning the mechanical properties of the materials for desired applications. Scherman and co-workers prepared a supramolecular hydrogel through ternary complex formation between the host CB8 and multivalent hydrophilic copolymers bearing either pendant methyl viologen or naphthoxy derivatives which are favourable guests for CB8.[51] When CB8 was added to colourless aqueous solutions

of the polymers bearing the guests, a highly viscous, coloured supramolecular hydrogel was obtained. The degree of cross-linking can be controlled by varying the concentration of CB8 added. The resulting supramolecular hydrogel was found to be stimuli responsive and its properties can be tuned by external stimuli such as heat. It also exhibited thermal reversibility and subsequent facile modulation of microstructure upon further addition of CB8 and thermal treatment. The mechanical property of this hydrogel is comparable to existing supramolecular hydrogels.

Using the same idea of ternary complex formation ability of CB8 with MV^{2+} and naphthoxy derivatives, ultrahigh-water-content (up to 99.7% water by weight) supramolecular hydrogels exhibiting multistimuli responsiveness were reported (Fig. 9).[52] For this purpose first cellulosic derivatives and poly(vinyl alcohol) were decorated with MV^{2+} and naphthoxy binding motifs. When these polymers which contain 90% cellulosic solid content, were mixed with CB8, an immediate formation of a coloured, transparent hydrogel was observed. The mechanical properties of these hydrogels can be controllable owing the cross-links of non-covalent bonding and also this important feature allows for rapid self-healing of the materials after damage caused by deformation. Most importantly, these hydrogels are responsive to a number of external stimuli including temperature, chemical potential, and competing guests.

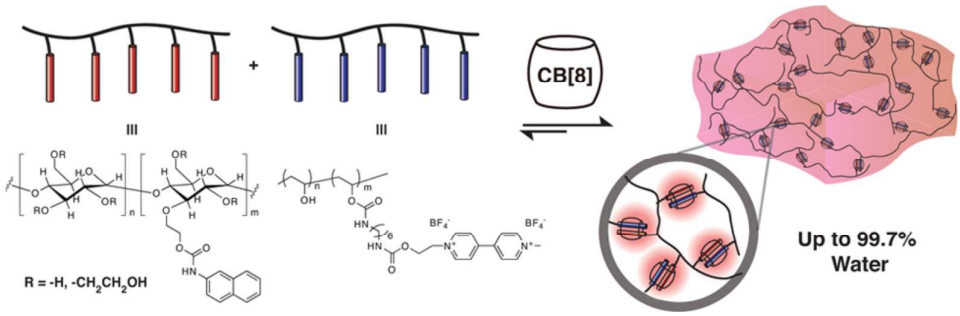


Fig. 9 The preparation of the cellulosic hydrogel with a water content of up to 99.7% in the presence of CB8. (Reprinted with permission from ref. 52. Copyright 2012 American Chemical Society.)

Similar approach was applied for the preparation of nanocomposite hydrogel which consists of hard and soft polymeric domains.[53] Hard segment was made up of cellulosic nanocrystals (CNCs) which are mechanically strong colloidal rods with nanometer-scale lateral dimensions and were functionalized with methacrylate polymer brushes bearing naphthyl units by surface-initiated atom transfer radical polymerization bearing naphthyl units. Soft segment was composed of poly/vinyl)alcohol functionalized with viologen units.

These domains can be bound together through supramolecular cross-links in the presence of CB8 in aqueous medium to form supramolecular nanocomposite hydrogels which have important features as high storage modulus, rapid sol–gel transition, and rapid self-healing even upon aging for several months.

Dynamically cross-linked networks were also prepared via recognition of amino acids by CB8.[54] In this work, water soluble styrenic monomers were copolymerised with synthetically derived aromatic amino acid monomers of phenylalanine and tryptophan which are good guest for CB8. The resulting polymers were shown to form dynamic and self-healing physically crosslinked hydrogels via recognition and binding of the amino acids to CB8. These materials have potential to be used in area such of tissue engineering to construct scaffolds.

Tan and co-workers reported the preparation of pH and thermo responsive supramolecular hydrogels based on the host-guest complexation of CB8 with the viologen units of poly(N-(4-vinylbenzyl)-4,4'-bipyridinium dichloride-co-acrylamide) (P4VBAM)s in water. The hydrogel formed in the basic aqueous medium in which CB8 could encapsulate two bipyridyl units to link the polymer chains. Reversibility could be achieved by adjusting the pH as well as by heating and cooling the system.

2.2.2 Supramolecular nanoparticles, micelles, vesicles

Single chain nanoparticles owing to their well-defined shape, size and composition are highly appealing for many applications including biomedicine and photonics. Host-guest chemistry of CB8 was utilized successfully in their preparation (Figure 10).[56] For this purpose, a range of poly(N-hydroxyethylacrylamide) polymers were prepared by ATRP and were functionalized using an isocyanate conjugation with guest moieties (MV^{2+} and Np) for complexation with CB8. The size and dispersity of the nanoparticles can be controlled by carefully tuning the concentration of polymers and CB8. Addition of CB8 to very dilute solution of polymers yield single chain polymer nanoparticle but in high concentration more than one chains collapse together to form large nanoparticles with a broad polydispersity index. When CB7 has been used which has a smaller cavity than CB8 and cannot accommodate two guests at the same time, nanoparticle formation was not observed proving further the formation of ternary complex between the guests located at the termini of polymers and the host CB8.

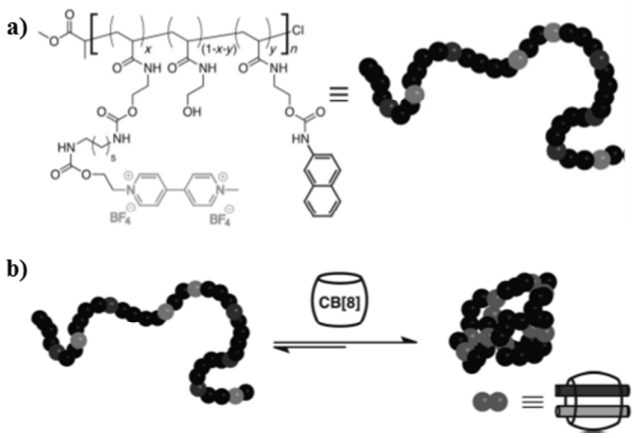


Fig. 10 (a) The structure of poly(N-hydroxyethyl acrylamide) polymer conjugated with guest moieties (MV^{2+} and Np) for complexation with CB8; **(b)** Single chain polymer nanoparticle formation through ternary complex of CB8. (Reprinted with permission from ref. 56. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.)

Using supramolecular approach core–shell polymeric microspheres with a cleavable shell were prepared in water.[57] In this study the core component is based on a MV-functionalised polymeric microsphere and the shell is composed of Np-functionalised linear acrylate polymers containing hydrophilic oligoethylene glycol units and/or rhodamine-B units. Core and shell components were linked together through ternary complex formation between CB8 and the residues of Np and MV^{2+}. The shell can be easily cleaved by introducing a competitive guest which has a higher affinity toward CB8 than the existing guests on the system. These cleavable core-shell nanoparticles could have potential applications in the area of cancer therapy because the toxicity of nano/microparticles could be switched on demand.

Supramolecular stimuli-responsive, reversible micelles[58] that can be used for encapsulation of anticancer drug and controlled drug release were reported.[59] In the preparation of this system, double hydrophilic copolymers were used; one block was naphthalene-terminated poly(dimethylaminoethylmethacrylate) (PDMAEMA) bearing as a pH-responsive segment and second one was methylviologen terminated poly(N-isopropylacrylamide) (PNIPAAm) as a temperature-responsive block. Mixing aqueous solutions of these two polymers in the presence of CB8, they were bound together to form micelles. The cargo of the pH-responsive nanocontainers can be unloaded through pH-triggered release within endosomal and lysosomal vesicles at around pH 4, whereas temperature-responsive nanocontainers are suitable for triggering via remote heating methods

such as infrared irradiation. The molecular weights of the polymers were kept below 10000 g/mol in order to facilitate the excretion via renal filtration after releasing cargo.

When drugs are loaded into micelles through non-covalent interactions, there may be some drawbacks as drugs might be released prematurely. Thus, conjugating the drugs to the micelle forming polymeric chains through a covalent bond that can be cleaved under an appropriate stimulus could improve the performance of the micelles. In this context, Wang et al prepared pH responsive supramolecular prodrug micelles based on CB8 for intracellular drug delivery (Fig.11).[60]

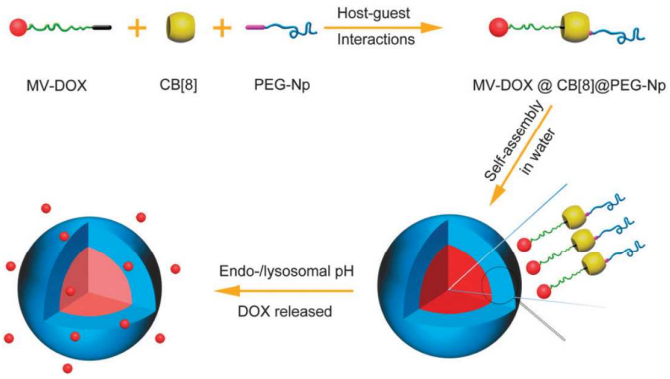


Fig.11 Schematic of the formation of supramolecular prodrug micelles trough ternary complexation and controlled release of DOX by endo-/lysosomal pH stimulus. (Reprinted with permission from ref. 60. Copyright 2014 Royal Society of Chemistry.)

To form micelles, they synthesized naphthalene-terminated poly(ethylene glycol) (PEO-Np) and methyl viologen conjugated doxorubicin (MV-DOX). Aqueous solutions of PEO-Np, MV-DOX, and CB8 were mixed in an equimolar ratio to form ternary complex. Consequently, these amphiphilic ternary structures were self-assembled in water to form micellar structures. In the absence of doxorubicin, no micelle formation was observed meaning that doxorubicin is essential to provide hydrophobicity required for the micelle formation. DOX units were linked to polymer chains through hydrozone bonds which could be cleaved under acidic medium. Faster drug release was observed at pH 5 than the physiological pH 7.4 when micelles were exposed to the aqueous solutions of buffers at pH 5 and pH 7.4.

Supramolecular peptide amphiphile vesicles were prepared in water through host–guest complexation of CB8.[61] First amphiphiles were prepared; for this, a simple peptide sequence was decorated with pyrene which will act as one of the guests for CB8 as well as a fluorescent sensor and the viologen unit as a second guest was linked to a long hydrophobic tail. Vesicles were formed by the self-assembly of the prepared amphiphiles in water. The vesicles are reversible and their disassembly process could be triggered by competitive guests such as 2,6-dihydroxynaphthalene and 1-adamantylamine. Upon the disassembly of vesicles, pyrene attached peptides are released into the surrounding environment and this, in turn, causes the simultaneously a "switch on" of the fluorescence of pyrene units. Vesicles were characterized by TEM and DLS and their diameters found to be around 200 ± 60 nm. In vitro cell assays showed that these vesicles were readily taken up by HeLa cells and responded to multiple external triggers indicating that their toxicity could be regulated using an appropriate stimulus.

These peptide amphiphile vesicles were also utilized for the encapsulation of basic fibroblast growth factor.[62] However, the vesicles used in this work contained PNIPAAm terminated with methyl viologen instead of long hydrophobic alkyl chain. Ternary complexation formed between short peptide terminated with first guest pyrene and methyl viologen terminated PNIPAAm and this led to formation of amphiphile which self-assembles into vesicles at physiological temperature.

2.2.3 Supramolecular colloidosomes

Very recently Sherman et al. reported on the preparation of supramolecular colloidosomes.[63] Colloidosomes are microcapsules whose shells are composed of self-assembled colloidal nanoparticles. These colloidal nanoparticles are either fused together by thermal treatment or cross-link to achieve stable but permeable surface. In this work, authors first formed monodisperse oil droplets using microfluidic technique and then the polystyrene based nanoparticles which are decorated with binding motifs of MV for CB8 are self-assembled at the water-oil droplet interface. The PS-MV particles were reversibly cross-linked with a copolymer of poly(N,Ndimethylacrylamide), comprising 10 mol% of naphthol-modified hydroxyethylacrylamide (p-Np, 10.1 kDa) via a supramolecular complex of CB8. They also demonstrated the ability of these capsules to encapsulate, retain and subsequently trigger the release of cargo through disassembly of the ternary supramolecular complex which was achieved by introducing 1-adamantylamine (ADA) as a competitive guest for CB8. ADA

forms a strong 1:1 complex with CB8, with displacement of the methyl viologen and naphthol moieties (Fig. 12).

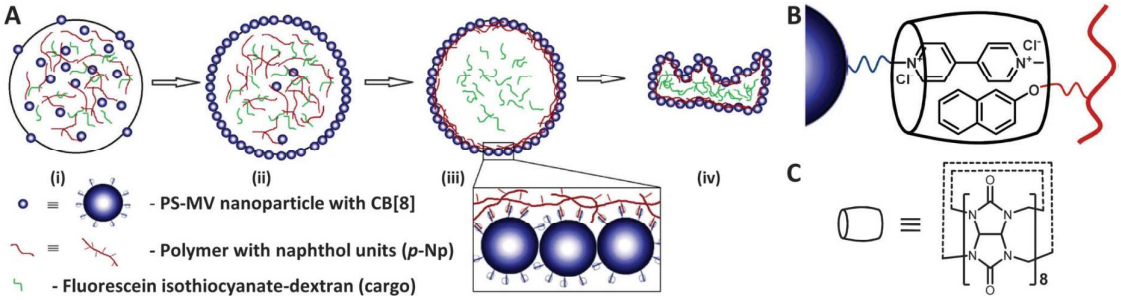


Fig. 12 (A) Schematic of colloidosome formation; (B) ternary supramolecular complex formation between PS-MV, p-Np and CB8. (C) The molecular structure of CB8. (Reprinted with permission from ref. 63. Copyright 2014 Royal Society of Chemistry.)

2.2.4 Ordered supramolecular arrays

Supramolecular approach was also employed for functionalization and patterning of gold surfaces.[64] This was realized by self-assembled monolayers of viologen unit linked decanethiol which is one of the guests for CB8 were formed on the gold substrate and then the polymeric nanoparticles composed of the copolymer of styrene, vinyl styrene and 2-naphthyl methacrylate were introduced to immobilize these monodispersed polymeric particles onto the surface through ternary complex formation of CB8 with guest one and guest 2 as shown in Fig. 13. Using this approach, it is also possible to prepare patterned colloidal arrays.

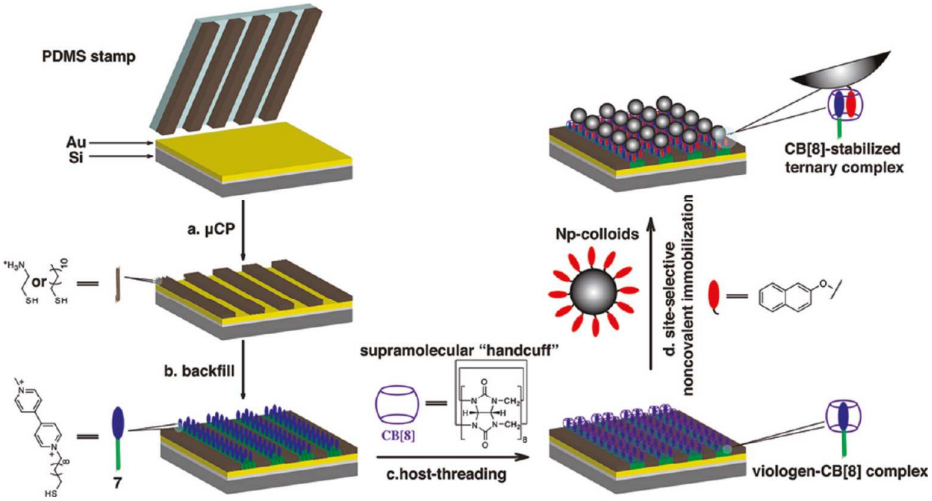


Fig. 13 Schematic representation of site-selective noncovalent immobilization of Np-colloids on a micropatterned viologen terminated Au substrate in the presence of CB8. (Reprinted with permission from ref. 64. Copyright 2010 American Chemical Society.)

In another work, multi stimuli responsive, reversible supramolecular system was constructed employing both redox and light-responsive guests such as viologen and azobenzene derivatives.[65] This system might find practical applications in the fabrication of memory devices. Hetero ternary complexes formed between these guests and CB8 through host-guest chemistry. To show the practicality of this approach and visualize the process, patterned surfaces were prepared by micro contact printing of thiol-containing azobenzene derivative on Au substrate. When the complexes of CB8 with fluorescein attached viologen were introduced in water, a heteroternary complex formation takes place and the process can be clearly monitored due to the presence of the fluorophore in the system. The system can be made reversible irradiating with light due to conformational changes of azobenzene derivatives from trans to cis isomer.

Li et al designed and synthesized CB8-mediated single-layer two-dimensional honeycomb supramolecular organic framework (SOF) in water.[66] 4,4′-bipyridin-1-ium (BP) units and hydrophilic bis(2-hydroxyethyl)carbamoyl groups were linked to 1,3,5-triphenylbenzene core to suppress 1D stacking of the triangular backbone and to ensure solubility in water. When CB8 was added to this triangular core molecule, 2D-network was obtained because of homoternary complex formation between two BP units and CB8 (Fig. 14). This 2D framework has been characterized by various ^{1}H NMR spectroscopy, dynamic light scattering, X-ray diffraction and scattering, scanning probe and electron microscope techniques and by comparing with the self-assembled structures of the control systems.

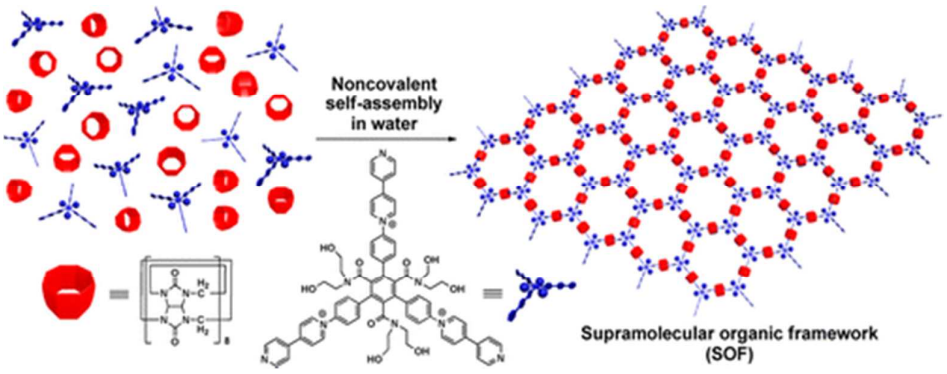


Fig. 14 Schematic representation of CB8-mediated single-layer two-dimensional honeycomb supramolecular organic framework (SOF) fromation in water. (Reprinted with permission from ref. 66. Copyright 2013 American Chemical Society.)

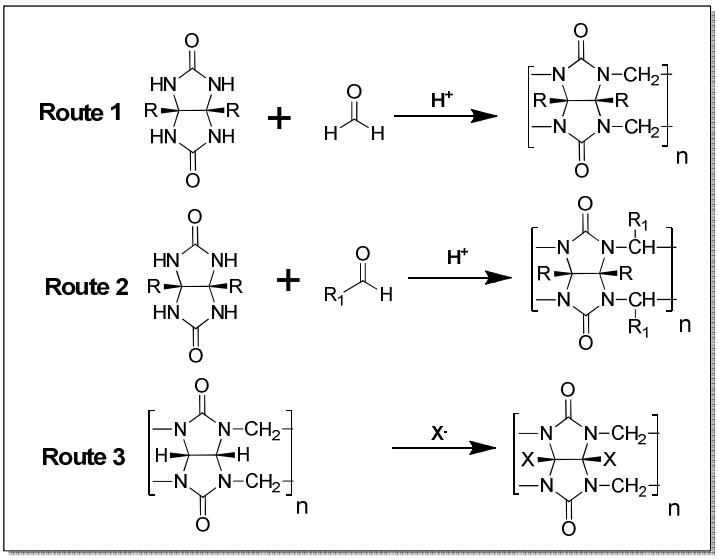
In a slightly different design SOF was prepared in such a way that viologen units attached triangular building block was utilized and SOF formed by the dimerization of viologen radical cation units in the presence of CB8.[67] The resultant supramolecular networks have been characterized by various techniques including UV-vis absorption sepctroscopy, electron paramagnetic resonance, dynamic light scattering, solution and solid phase small angle X-ray diffraction, and AFM experiments.

It was also shown that CB8-based organic crystals with well-defined micro- and nanostructures could be prepared through host-guest chemistry of CB8 with small organic molecules.[68] Using this approach, it is possible to control the shape, morphology and composition of the crystals. Especially when the optically active guests are used in their preparation, the resultant crystals might find interesting applications in the area of photonics and in the solid state laser applications.

3. CB-based nanostructures constructed from surface functionalized CB homologous

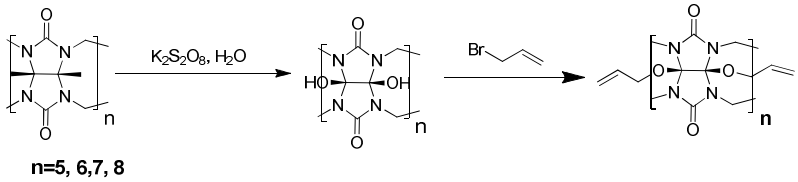
Although functionalized CBs could find many potential applications in the area of nanostructured materials, their functionalization have been challenging and thus limit their use for further applications.[69] In recent years there have been many efforts on attaching functional groups especially on the periphery of cucurbiturils. Mainly three different routes have been adopted for this purpose.[70-72]

Route 1 involves the use of glycoluril containing functional groups on the equatorial positions before condensing with aldehyde to form CBs (Scheme 1: Route 1).[70] However this method results in various mixtures of substituted and unsubstituted CBs which are almost impossible to separate. Another method is to functionalize the aldehyde and then condense to form the CBs (Route 2). At first this method was reported to be unsuccessful however Sindelar and co-workers recently reported the functionalized CB6 on the methylene bridge starting from functionalized aldehyde.[71] Many attempts to directly functionalize CBs failed because of their high chemical stability. Kim and co-workers developed a method to post functionalize CBs directly with hydroxyl groups (Route 3).[72]



Scheme 1 Different routes of CB functionalization

This method involves reaction of CB (n = 5–8) with potassium persulfate ($K_2S_2O_8$) in water to yield perhydroxy-CB[n], $(HO)_{2n}$CB[n] (n =5–8) as potassium ion complexes (Scheme 2).[72] The typical yield for the lower homologues CB5 and CB6 is in the range 40–45% and 5% or less for the higher homologues CB7 and CB8. This decrease in yield could be explained by the instability of the perhydroxylated products. The mechanism of CB hydroxylation is not fully understood although an OH radical generated by $K_2S_2O_8$ is expected to be involved. X-ray data revealed the presence of hydroxyl groups at the periphery of the CB $(HO)_{12}$CB[6] and $(HO)_{10}$CB[5]. These hydroxy derivatives of CB[n]s are reported to be soluble in both DMF and DMSO. The perhydroxy CB[n]s can further be functionalized with other functional groups via simple organic synthesis to obtain desired functional groups on CB[n]s as shown in Scheme 2.



Scheme 2 Synthesis of perhydroxy CBs and allyoxy-CBs.

Although fully substituted CB[n]s have great potential applications, attaching single functional group on the parent CB[n] would guarantee a high level of control over molecular structures and topologies on the nanoscale. Several routes have been reported to synthesize

mono functionalized CBs starting with functionalized glycoluril or functionalized aldehyde. However these methods involve very tedious separation techniques. Sherman and co-workers reported the first method to directly mono functionalized CB[6].[73]Although the MonOH is more soluble in water compared to the parent CB[6], the solubility of MonOH in water is still not so great. This can be explained by the isostructure of MonOH with the parent CB[6] structure as suggested by the crystal structure of MonOH as $MonOH.2Na_2SO_4.23H_2O$. The mono functionalized CB[6] can further be functionalized with reactive functional groups. Very recently Kim and co-workers reported the isolation of mono hydroxyl functionalized CB7 by slightly modifying the synthetic reaction conditions used for the synthesis of perhydroxyCB[n].[74]

Although post-surface functionalized CBs with reactive functional groups are very useful building blocks in the assembly of supramolecular structures, there are only a handful of examples. The following section will accordingly discuss the examples where the post-fucntionalized CBs were involved in the construction of nanoparticles, nanocapsules, and nanosheets.

3.1 Nanocapsules

Polimeric nanocapsules were prepared through a facile, template-free synthetic method using a well-designed, rigid and disk-shaped CB-based building blocks.[75] CB6 fully functionalized with allyoxy groups were polymerized through thiol-ene click chemistry irradiating with light to from nanocapsules. The mechanism of their formation was suggested as first formation of 2D-network which turns into a cap and then a hollow sphere. This was also supported by theoretical calculations.

The cavity of CBs are available for sequestering the suitable sized-hydrophobic molecules; this feature makes the polymer nanocapsules potentially useful in many applications including targeted delivery and imaging. Moreover, the surfaces of the nanocapsules could be decorated with many useful reactive groups through host-guest chemistry. To demonstrate this, fluorescent probes linked to spermidine were attached to nanocapsule surfaces via non-covalent interactions and the nanocapsules were imaged using confocal laser scanning microscopy (Fig. 15).

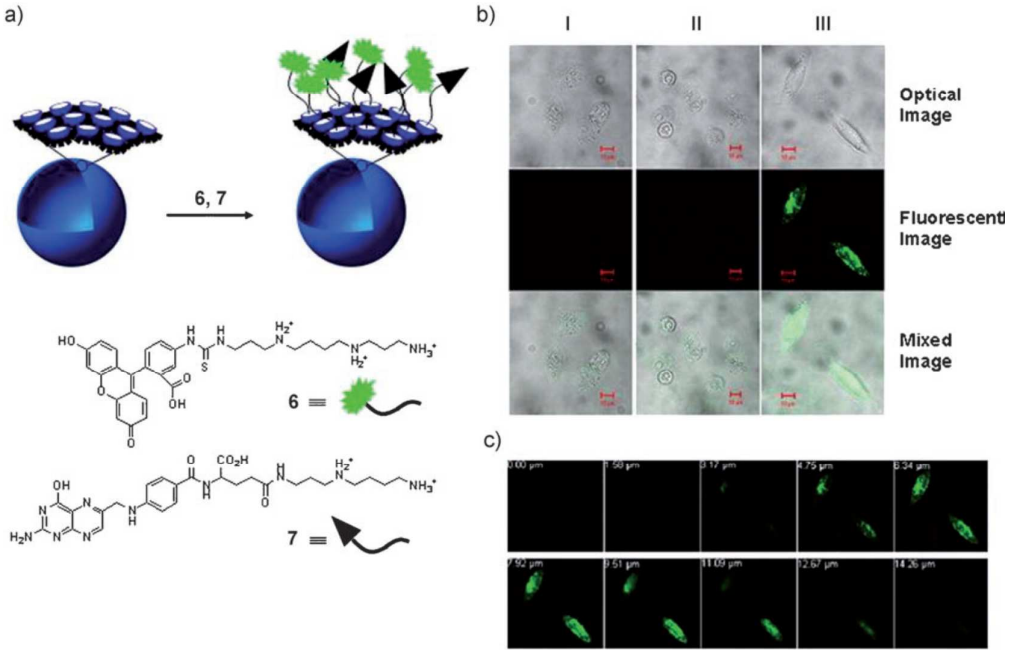


Fig.15 Preparation of surface-decorated polymer nanocapsules and confocal microscopy images of the polymer nanocapsules incorporated into KB cells. (Reprinted with permission from ref. 75. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.)

Second-generation CB-based nanocapsules were synthesized using a slightly different design than the previous one and have potential to be used in the controlled cargo delivery. They were programmed to release loaded cargos in a reducing environment due to the presence of reducible disulfide bridges in their structures.[76] For their synthesis, first hydroxyl groups of allyoxy-CB6 were treated with mercaptoethylamine to obtain disk shaped-rigid CB-based building blocks and then, upon addition of disulfide containing bifunctional active ester, 2D-polymeric networks were formed via amide bond formation which gradually curved into spherical nanocapsules. The nanocapsule formation was supported by high resolution TEM (HRTEM) images showing that they have an average diameter of 50-90 nm with hollow interior (Fig. 16).

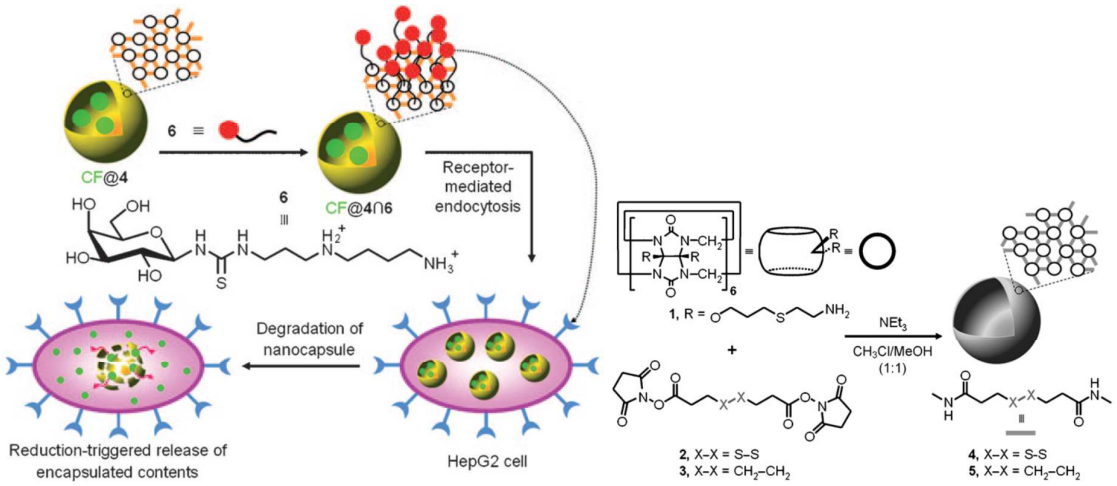


Fig.16 Schematic representation of the surface modification of CF-loaded nanocapsule with galactose-spermidine through host–guest interactions, the receptor-mediated endocytosis, and the reduction-triggered release of the encapsulated CF to cytosol. (Reprinted with permission from ref. 76. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.)

In order to demonstrate the applicability of polymer nanocapsules in a controlled-drug release, carboxyfluorescein (CF) encapsulated nanocapsules were prepared and the surface of the nanocapsules were decorated with galactose-spermidine to target over-expressed galactose receptors in HepG2 hepatocellular carcinoma cells. The internalization and reduction-triggered release of the fluorescent dyes from the capsules monitored by confocal microscopy and the results were compared with the capsules loaded with fluorescent dyes but they do not have reducible disulfide linkage in their structures. When reducible nanocapsules were internalized by the cells, an increase in the fluorescent emission was observed due the cleavage of disulfide linkage and the release of the fluorescent of dyes into the cytoplasm. However, in the case of non-reducible nanoparticles loaded with dyes, there was no increase in the fluorescent emission indicating that the dyes were tightly kept inside the nanocapsules.

It was also shown that these nanocapsules could be decorated with metal nanoparticles (M=Pd, Au, and Pt). The sulphur residues as well as carbonyl groups of CBs on the surface of the nanocapsules could act as ligands to stabilize these metal nanoparticles. Catalytic ability of the Pd-nanoparticle decorated nanocapsules were demonstrated successfully in the Suzuki coupling and the Buchwald–Hartwig amination reaction.[77]

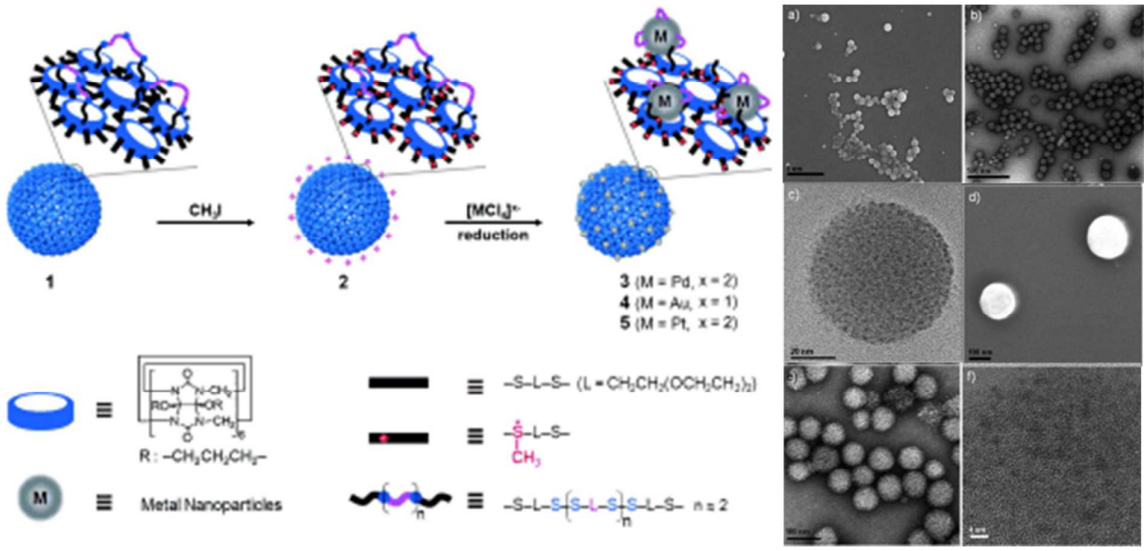


Fig. 17 Schematic presentation of the preparation of CB6-based nanocapsules decorated with metal nanoparticles (M=Pd, Au, and Pt) and TEM images of these hybrid nanocapsules. (Reprinted with permission from ref. 77. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.)

3.2 Nanosheets

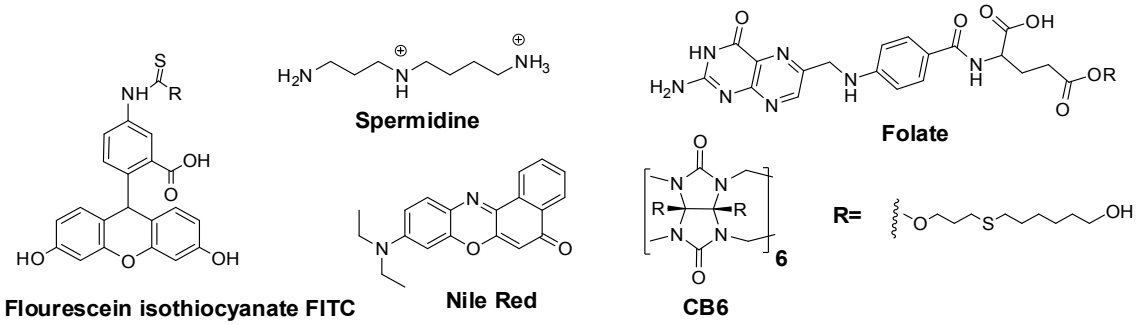
As mentioned above during the formation of nanocapsules, first 2D-polymeric network types structures form and then, this structures become cap-like structure and finally spherical hollow nanocapsules. Kim and co-workers carefully investigated the formation of 2D-networks by tuning the reaction conditions.[78] They observed especially bending rigidity of building blocks and the solvent play an important role whether 2D-networks formation will lead to nanocapsules or these networks will simply fold or curve not forming hollow nanocapsules. From the theoretical and experimental studies they concluded that while poor solvent and building blocks with low bending rigidity allow nanocapsule formation, good solvent and high bending rigidity cause the formation of rolled 2D-polymeric structures. $(Allyloxy)_{12}CB6$ was cross-linked with 1,2- ethanedithiol through thiol-ene click chemistry irradiating with light to form 2D-networks in DMF which is a good solvent for the building blocks. In order to obtain free-standing, monolayered films the layers should not stack

together. To achieve this, they added protonated spermine which bind to CBs and provide positively charged surfaces that will cause repulsion between the polymer film layers keeping them apart. These free standing, one molecular thick polymeric films are very appealing and might find many important applications spanning from selective separation, transport and sensing.

The formation of vesicles and nanocapsules were also reported by a post-functionalization of the surfaces of CB6 with polymers using radical initiator. Polyacrylamide grafted onto equatorial position of the CB6 was prepared using potassium persulfate as initiator and oxidant. These polyacrylamide grafted CBs were self-assembled into vesicles and the formation of the vesicles were confirmed by microscopic techniques including AFM, SEM and TEM.[79]

3.3 Nanoparticles

Functionalized CB6 was utilized in the preparation of nanoparticles to make use of their cavity for carrying hydrophobic drugs or modifying their surface in targeting drug delivery.[80] Perhydroxy-CB6 was first converted into $(allyloxy)_{12}$CB6 and subsequently 6-mercaptohexanol was attached through thiol-ene click chemistry. The functionalized CB6 was dissolved in water and while sonication minimum volume of ethanol was added to induce the nanoparticle formation. Resulting nanoparticles were characterized with DLS and TEM techniques. Folate receptor, Fluorescein isothiocyanate (FITC) and Nile Red (NR) as fluorescent tags for optical imaging were first attached to spermidine derivatives in order to incorporate them onto the surfaces of nanoparticles through host-guest chemistry of CBs. The molecular structures of Nile Red, folate receptor, spermidine, functionalized CB6 are shown in Scheme 3. With and without folate receptor attached functionalized CB6 nanoparticles loaded with anti-cancer drugs such as paclitaxel (PTX) were also prepared and HeLa cells were incubated with these drug loaded nanoparticles. IC_{50} (50% of cell growth inhibition concentration) values were calculated as 1.24 ±0.20 μg-mL^{-1}, 0.33±0.10 μg-mL^{-1}, 0.08±0.02 μg-mL^{-1}; for free PTX, PTX-CB6NPs, PTX-CB6NP-folate receptor, respectively. It can be concluded that CB6-NPs are remarkably effective even with nonspecific internalization of the drugs into the cytoplasm. Folate receptor also indicates enhanced cytotoxicity due to the receptor mediated endocytosis. These results represent the promising usage of functionalized CB6 nanoparticles for pharmokinetic effect of the drugs.



Scheme 3 Structure of Nile Red, folate receptor, spermidine, functionalized CB6 for nanoparticles synthesis.

3.4 Supramolecular scaffolds

Surface functionalized CB6-based supramolecular hyaluronic acid (HA) hydrogels for tissue engineering applications were described by Kim et al.[81] In order to mimic an extracellular matrix, functionalized CB6s were attached to HA and mixed with diaminohexane conjugated HA (DAH-HA) (Fig. 18). Due to high affinity of diaminohexane units toward CB6, the supramolecular hydrogel formed and served as an extracellular matrix which allowed the cell proliferation and exhibited no cytotoxicity. Cell growth process and the stability of the matrix could also be monitored by confocal laser microscopy incorporating fluorescent tags to the system through host-guest chemistry of CB6. *In situ* formation of supramolecular hydrogels under the skin of nude mice by sequential subcutaneous injections of CBs linked HA and diaminohexane conjugated HA solutions were also demonstrated. It was also shown that the hydrogel was biodegradable as enzymatic degradation occurred within 24 h after the treatment of hydrogel with hyaluronidase enzyme.

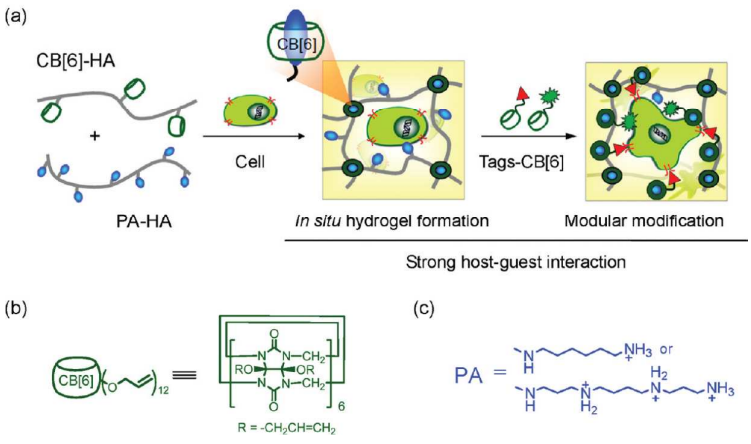


Fig. 18 (a) Schematics for the formation of supramolecular biocompatible hydrogel through host guest chemistry of CB6 attached to HA and diaminohexane or spermine conjugated HA. The chemical structures of (b) allyloxy-CB and (c) diaminohexane and spermine. (Reprinted with permission from ref. 81. Copyright 2012 American Chemical Society.)

Modifying the previously described approach,[81] supramolecular hydrogels were prepared as a scaffold with ability to deliver drug in controlled fashion for cartilage regeneration and other tissue engineering applications (Fig. 19).[82] For the preparation of hydrogel through host-guest chemistry of CB6, first two different hyalunaric acid (HA) derivatives were synthesized; one of them was prepared by attaching mono-allyoxy functionalized CB6 to HA via thiol-en chemistry and the second one contains diaminohexane units grafted to HA. Mixing these two HA derivatives in the presence of human mesenchymal stem cells (hMSCs) resulted in the formation of supramolecular cytocompatible hydrogels which had a highly porous microstructure. It was observed that more than 95% of the hMSCs in these HA hydrogels survived and proliferated even after incubation for 10 days. The differentiation of hMSCs was temporally controlled by changing the release profiles of transforming growth factor-β3 (TGF-β3) and/or dexamethasone (Dexa) from the hydrolyzable Dexa-CB6. The effective chondrogenic differentiation of hMSCs was confirmed by biochemical glycosaminoglycan content analysis, real-time quantitative PCR, histological, and immunohistochemical analyses.

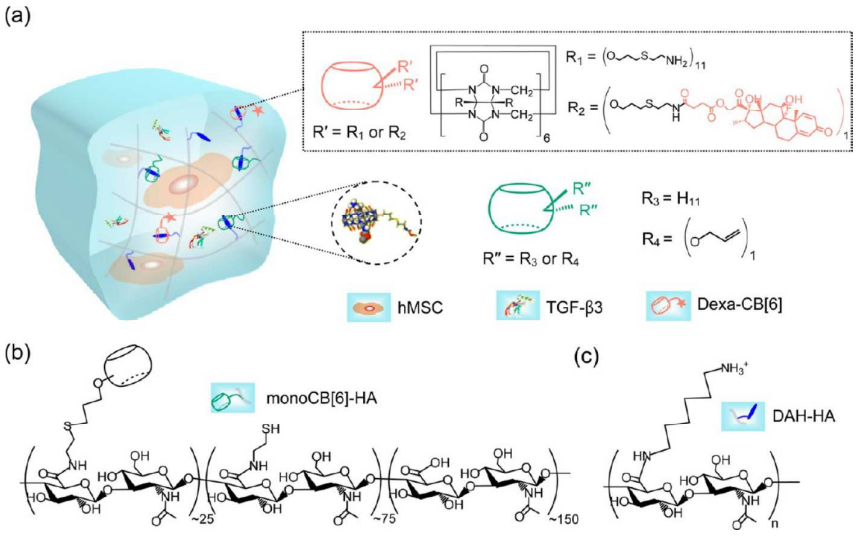


Fig. 19 Schematics of (a) supramolecular monoCB6/DAH-HA hydrogels encapsulating hMSCs and TGF-β3 with modularly modified Dexa-CB6 by the strong host−guest interaction

between CB6 and DAH. The chemical structures of (b) monoCB6-HA and (c) DAH-HA. (Reprinted with permission from ref. 82. Copyright 2014 American Chemical Society.)

4 Conclusions

In this review we presented a number of CB-containing nanostructures which were either constructed by host-guest chemistry of CB homologues or formed through the self-assembly of post-functionalized CB6 or CB7.

By taking advantage of the rich host-guest chemistry of CB homologous, a number of different nanostructures have been prepared. Especially the ability of CB8 to form ternary complexes with electron rich and electron deficient species has been well-exploited in the construction of supramolecular nanostructures such as supramolecular hydrogel, nanoparticles, vesicles, supramolecular arrays and so forth. These nanostructures could find many interesting applications especially in the area of self-healing materials, the delivery of drug or other therapeutic materials and the area of theranostics as well as for controlling the viscosity of materials.

Although post-surface functionalized CBs with reactive functional groups are very useful building blocks in the assembly of supramolecular structures, until recently especially mono-functionalization CB homologues have been proven to be challenging and thus limited their use for further applications. The yields are still quite low in the synthesis of perhydroxy or mono-hydroxy CBs which is another limiting factor for their wide applicability. As a result of the aforementioned reasons, the examples on the post-functionalized CB-based nanostructures are relatively scarce in the literature compared the non-functionalized CB-based nanostructures. Therefore, it is quite important to find new methods which would provide high yields for the synthesis of functionalized-CB homologues especially for CB7 and CB8 with large cavities.

In the coming days, we expect to see more works regarding the multi-functional nanostructures based on the post-functionalized CB homologues.

Acknowledgements

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Table of contents

Nanostructured materials including nanoparticles, nanocomposites, vesicles, rods and so forth have been prepared by taking advantage of the interesting features of cucurbituril homologues.