

Helical Colloidal Sphere Structures through Thermo-Reversible Co-Assembly with Molecular Microtubes**

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Self-assembly is ubiquitous in nature, science, and technology and provides a general route to achieve order from disorder at various length scales.^[1] Extensive effort has been exerted to molecular and colloidal self-assembly, where molecules and colloids, respectively, organize into larger-scale ordered structures. Although these two research areas have developed separately to a great extent, their combination would be very promising. Nature, for instance, utilizes hierarchical self-assembly across different length scales to construct complex, dynamic functional entities such as cells. Here we bridge the nano- and microscale by the hierarchical co-assembly between molecules and colloids, where molecular self-assembly induces the self-assembly of colloids into ordered structures.

Colloidal self-assembly is widely employed in analogues of molecular systems and processes encountered in chemistry, physics, and biology.^[2–11] Colloids mimic naturally occurring systems such as microorganisms,^[10] micelles,^[3] molecules,^[6] and polymers.^[7] The directed organization into such specific ordered structures is fuelled by the rapidly advancing availability of colloidal building blocks that are asymmetric in shape and chemical functionality.^[2–6,12] Of particular interest is the creation of colloidal helical structures, for instance, as models of the DNA helix. Colloidal structures with a helical twist have been assembled from complex anisotropic magnetic colloids^[4] and amphiphilic Janus spheres.^[5] These sophisticated building blocks are believed to be essential for inducing directionality and chirality in self-assembly.^[13]

Here we demonstrate that the simplest of building blocks, namely the isotropic sphere, already suffices to generate a library of ordered structures, including helical sphere chains. These structures form through the spontaneous co-assembly of colloidal spheres and confining surfactant–cyclodextrin microtubes,^[14] thereby coupling molecular and colloidal self-assembly. We introduce these microtubes as a novel versatile platform for the self-assembly of colloid-in-tube structures, as depicted in Figure 1 a. Microtube precursors sodium dodecyl sulfate (SDS) and β -cyclodextrin (β -CD) are mixed with colloidal particles at elevated temperatures to obtain isotropic mixtures (see the Supporting Information for experimental details). The microtubes form upon cooling to room temperature and, simultaneously, the colloids co-assemble inside the microtubes into ordered, chain-like structures throughout the sample volume. The elementary building block of the straight and rigid microtubes consists of one SDS molecule and two β -cyclodextrin molecules, forming an aqueous inclusion complex (Figure 1 a). These building blocks in turn assemble into multiple curved SDS/ β -CD bilayers with in-plane order, thereby forming a set of coaxial hollow cylinders. The thus formed microtubes exhibit a rather uniform pore diameter of 0.9 μm and prefer to align parallel with each other (Figure 1 b,c). The colloidal structures are induced by the microtubes, which act as a cylindrically confining environment for the colloids.

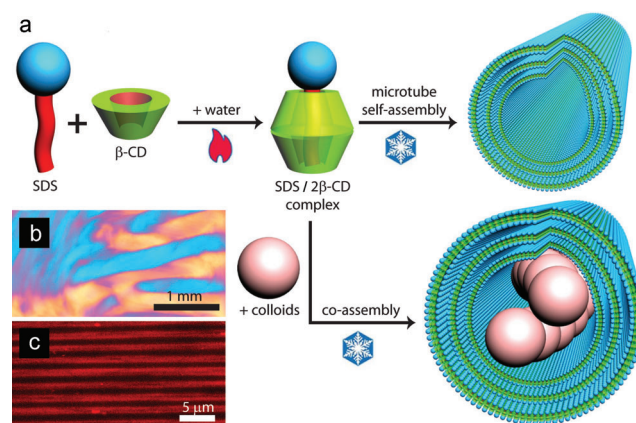


Figure 1. Co-assembly of colloids and microtubes. a) Representation of the self-assembly of SDS/ β -CD (sodium dodecyl sulfate/ β -cyclodextrin) inclusion complexes into microtubes, incorporating and structuring spherical colloids in their cylindrical cavities. b, c) The straight and uniform SDS/ β -CD microtubes align parallel with each other, as evidenced by polarized light microscopy (b, showing birefringence) and confocal laser scanning microscopy (CLSM; c, the microtube walls are fluorescently labeled by Nile Red).

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Our findings match the prediction that isotropic spheres may form helical structures upon cylindrical confinement.^[15] This simple geometrical approach is of relevance for much more complex phenomena such as protein folding.^[16] The only thoroughly studied system to date where nanoscale spheres assemble in cylinders into well-defined structures consists of carbon nanotubes that contain encapsulated fullerenes or other molecules inside the cylindrical nanopores.^[17] However, the small size of the objects and the harsh conditions required for their formation obstruct the direct visualization of the encapsulation of molecules and their dynamics. Additionally, the structures are formed by an irreversible assembly process. In principle, these limitations can be overcome by using colloids. In a limited number of studies, helical and related chain structures were generated from colloidal spheres.^[18] However, in none of these studies the assembly process was followed in time, and the structures obtained were mostly static, irreversible, and produced in a low yield. Moreover, the confining cylinders were not formed by self-assembly.

In contrast, with our co-assembly approach colloid-in-tube structures and their Brownian dynamics can be visualized *in situ* at the single-particle level. In addition, this molecular colloidal co-assembly is thermo-reversible, thus allowing for switching from the formation of colloid-in-tube structures to their disassembly within a narrow temperature range. Furthermore, the co-assembly is generic for colloids from different materials and is tunable through the tube-sphere diameter ratio. The colloidal sphere chains constitute an interesting model system for investigating structure and dynamics of colloids confined in 1D, while the thermo-reversibility provides a novel route to triggered particle release.

The diameter ratio between colloids and cylinders has a pronounced effect on the structure and dynamics of the eventual colloidal chains.^[15] Silica spheres with diameter $D = 790$ nm almost exclusively assemble inside the pores of the microtubes (Figure 2a and Supplementary Video 1). The spheres are predominantly arranged in straight single-particle chains that are subject to thermal motion. A small fraction of the spheres are present as mobile individual particles. The diversity of colloidal architectures that can be realized increases for smaller spheres. Colloid-in-tube assemblies from spheres with diameters of 508 nm display various ordered configurations (Figure 2b and Supplementary Video 2). These structures include particle chains with helical, zigzag, and zipper configurations, where closely packed zigzag structures are referred to as zipper chains. More closely packed structures are observed at higher local particle

concentrations. Spheres much smaller than the tube diameter do not form ordered structures and are randomly distributed (Figure 2c). In this case the microtubes cannot impose a structure-inducing confinement on the spheres.

We corroborated that the observed structures are generic for the spherical shape and are not related to the specific chemical nature of the colloids. To this end, we employed not only silica, but also polystyrene (PS) spheres with a range of sphere sizes. The largest PS spheres ($D = 1.88$ μm , Figure 2d) were larger than the microtube diameter and were used to test the effect of size exclusion. We confirmed that these spheres could not be incorporated into the cylindrical microtube pores, but were positioned outside the tubes as immobilized, mostly individual particles. Similar to silica spheres, PS spheres slightly smaller than the tube diameter mainly organize into straight single-particle chains (Figure 2e and Supplementary Video 3). The positioning of the particles along straight lines is strongly indicative of 1D in-tube assembly. Their motion is restricted to translations along the long axis of the pores and small lateral movements. Even smaller spheres ($D = 403$ nm) organize inside microtubes with high particle loadings into chains with characteristic zigzag patterns (Figure 2f), which can have different period lengths.

Interestingly, many of these zigzag and zipper chains gradually twist along their long axis and are, in fact, double-helical structures (Figure 3a). The pitch length over which a helical rotation takes place varies among the helices. We emphasize that these colloidal structures are realized by using

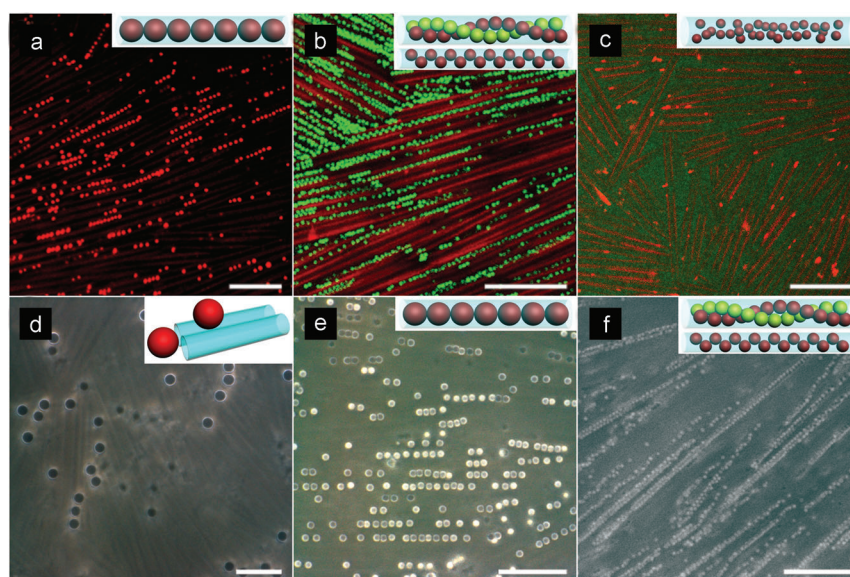


Figure 2. Size-dependent arrangement of colloidal silica and polystyrene (PS) spheres in microtubes with a uniform mean pore size of 0.9 μm , as revealed by CLSM (a–c) and optical microscopy images (d–f). a) Silica spheres ($D = 790$ nm) form dynamic, straight single-particle colloidal chains; see also Supplementary Video 1. b) Silica spheres ($D = 508$ nm) arrange into colloidal chains with helical, zigzag, and zipper configurations (Supplementary Video 2). c) Disordered distributions are obtained for small silica spheres ($D = 200$ nm). In (a–c), microtube walls are labeled with Nile Red, and silica spheres are labeled with rhodamine isothiocyanate (RITC) red in (a) and with fluorescein isothiocyanate (FITC) green in (b, c). d) PS spheres ($D = 1.88$ μm) larger than the microtube pores do not form ordered structures, but are immobilized and excluded from the pores. e) As in (a), but for PS spheres with $D = 812$ nm (Supplementary Video 3). f) PS spheres ($D = 403$ nm) organize in helical and zipper-like colloidal chains. Scale bars are 10 μm .

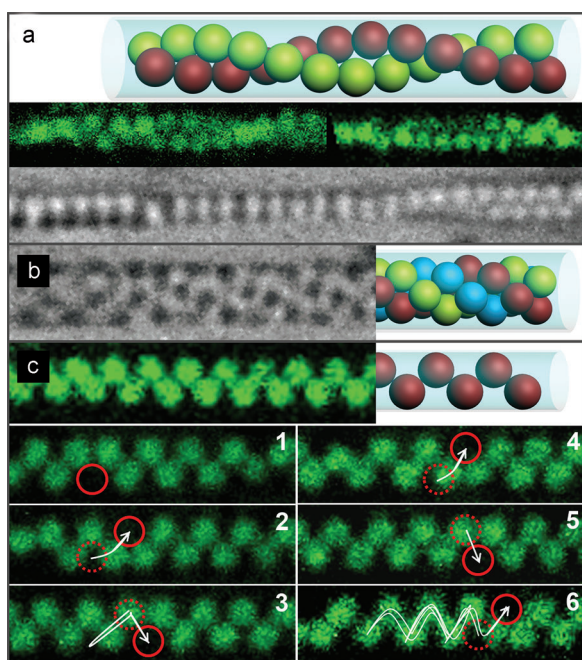


Figure 3. Helical and zigzag colloidal structures from cylindrically confined colloidal spheres. Microscopy images and schematic representations of ordered colloidal chains with different chain morphologies from PS ($D = 403$ nm; see gray-scale optical microscopy images) and silica ($D = 508$ nm; green spheres in CLSM images) spheres. a, b) Double (a) and triple helices (b) assembled from isotropic colloids. c) Dynamic zigzag configurations and time series (interval time 0.7 s for each turn in the white trajectory line) displaying the movement of a vacancy, marked by a red circle, along the chain.

colloids that are isotropic in shape and chemistry. The helical configuration imposed on the colloids is solely due to the confining microtubular environment. Furthermore, helices from three intertwining colloidal chains are generated (Figure 3b). The observed double and triple helices, with respective tube–sphere size ratios of 2.0–2.2 and 2.5, match the predicted structures.^[15]

Since the colloids are subject to Brownian motion, configurations are in dynamic equilibrium and can be considered as “living chains”. Hence, chain structures may interchange by the attachment and release of spheres, although the mobility of dense colloidal chains is restricted. Figure 3c illustrates the dynamic nature of colloidal structures for a zigzag chain with a vacant position (tube–sphere ratio = 1.8). The vacancy defect moves along the zigzag chain through the motion and exchange of spheres. The white arrows and lines indicate the pathway of the vacancy, eventually moving from left to right. Defect displacements along the chain are preceded by multiple, random forward and backward movements.

A unique feature of our system is the thermal reversibility of the co-assembly, since both molecular microtubes and colloidal chains disassemble and transform to an isotropic state upon heating and reassemble upon cooling. Careful thermal examination is vital to disclosing the mechanism behind colloid-in-tube assembly. The controlled thermal disassembly of microtubes and resulting disentanglement of

colloidal structures is illustrated in successive microscopic snapshots in Figure 4a,b (see also Supplementary Videos 4 and 5). The first image displays ordered colloidal arrangements at room temperature, while the fourth shows that the microtubes and colloids have become fully isotropic at elevated temperatures. The colloids become much more mobile upon heating, but their motion is still limited by the microtubes. Subsequently, a fraction of the microtubes melts and the colloid motion becomes more random, as it is no longer set by the tube walls. Some microtubes and enclosed chains remain intact for longer times. Most probably, the walls of these microtubes are thicker and consist of more SDS/ β -CD bilayers. Finally, the system becomes fully isotropic. All microtubes disassemble, and the colloids are released and undergo unrestricted Brownian motion.

An intriguing phenomenon during the melting process is highlighted in Figure 4b2, where some of the colloidal structures undergo a transition from straight to zigzag chain. Since the size of the spheres has not changed in this case, this observation must be related to a change in the microtubes. We hypothesize that the microtubes become more flexible upon heating and, consequently, can deform to accommodate the zigzag structure before complete disassembly.

To further demonstrate the thermo-reversibility of the assembly, we now complete the temperature cycle by cooling isotropic mixtures of SDS, β -CD, and colloids to room temperature. Figure 4c summarizes the reformation of the microtubes and colloidal configurations (Supplementary Video 6), which is typically completed in several minutes. The reassembly process is followed from the initial disordered state without microtubes, with colloids moving randomly throughout the sample volume. Next, the microtubes start to form, and the motion of the colloids is increasingly limited to one preferred direction, but the colloids have not yet realized their final configuration. At a temperature of approximately 35 °C the system suddenly slows down. The gelling SDS/ β -CD network, with the colloids embedded, drifts as a whole and comes to a halt. It should be noted, however, that not all microtubes nucleate at the same time. In Figure 4c2, for instance, several microtubes have already been formed, and incorporated colloids can only move within the micropores. Simultaneously, the motion of colloids in other areas is still random in all directions and is only limited by the outer walls of the early assembled microtubes. We believe that the non-uniform distribution of colloids over the microtubes is related to this microtube formation process. Microtubes that form early do not enclose many colloids. Subsequently, free space becomes more limited, while the colloid concentration in the remainder of the isotropic phase increases. Because there is no free space between the microtubes, the remaining colloids are then forced to be incorporated in microtubes with a higher colloid concentration. Since there is no exchange of colloids after complete colloid-in-tube assembly, every microtube may be regarded as an independent subsystem with different colloid concentration, structure, and dynamics.

The final stages of colloid ordering in Figure 5 shed more light on the co-assembly mechanism. Here, most microtubes have already formed and colloids are included in the cylindrical pores with a non-uniform distribution. The colloids

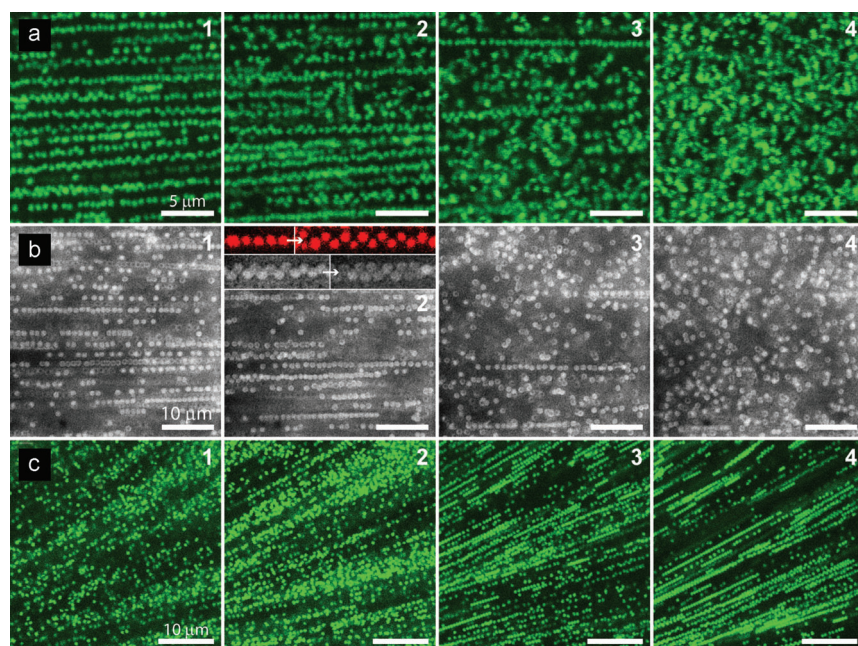


Figure 4. Thermo-reversibility of the co-assembly of colloids and microtubes. a, b) Colloid-in-tube structures disassemble and become isotropic upon melting of SDS/ β -CD microtubes at elevated temperatures ($T > 35^\circ\text{C}$). The stages of the melting process are shown in microscopy image sequences of colloidal chains from silica spheres ($D = 508\text{ nm}$; (a)) and PS spheres ($D = 812\text{ nm}$; (b)). The complete process can be seen in Supplementary Videos 4 and 5, respectively. The inset in (b2) depicts the transformation of straight single-particle chains to zigzag chains during heating, for both silica (top, red, $D = 790\text{ nm}$) and PS spheres. c) Colloid assembly into helical, zigzag, and zipper chains during formation of microtubes upon cooling isotropic SDS/ β -CD mixtures containing silica spheres ($D = 508\text{ nm}$, Supplementary Video 6).

self-assemble, while their configurations and dynamics are determined by the size of the colloids with respect to the tube diameter and the local colloid concentration. Colloidal chains grow by attachment of single colloids or other chains. 1D

volume, and its facile upscaling.

The colloidal chains constitute an interesting model system to further investigate the assembly, structure, and dynamics of a wide variety of colloids confined in 1D. Moreover, the co-assembly approach provides a novel route to the temperature-sensitive alignment and release of particles. In explorative experiments, we have shown that the number of possible colloidal configurations can be extended by the inclusion of anisotropic colloids. The thermo-reversible incorporation of colloids inside other surfactant–cyclodextrin hosts, including microtubes with different pore size, vesicles and lamellae,^[19] is another promising extension of the work reported here. We have shown that mixtures of simple and cheap building blocks may lead to well-controlled complex assemblies. In a broader perspective, we envision that the interplay between molecular and colloidal self-assembly may provide a fruitful pathway toward novel functional materials.

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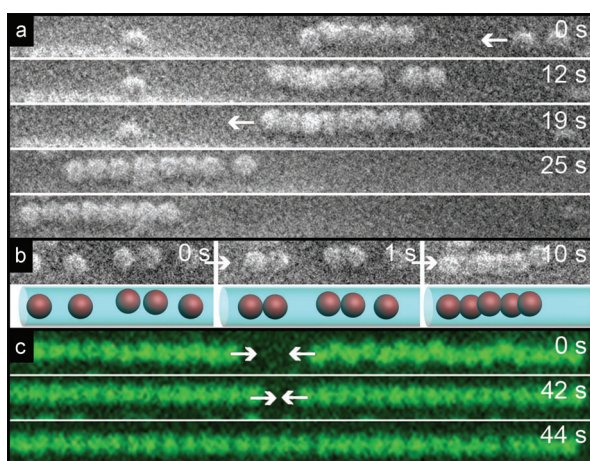


Figure 5. Final events of colloidal chain formation upon cooling. Colloids co-assemble with microtubes upon cooling isotropic SDS/ β -CD mixtures containing colloidal spheres. The late stages of the co-assembly process are characterized by growth of colloidal chains, distinctive unidirectional movement along the micropores, and fixation of the microtubes. This process was followed in time for polystyrene spheres (a, b, $D = 812\text{ nm}$) and silica spheres (c, $D = 508\text{ nm}$).

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