REVIEW ARTICLE

Creation of unique supramolecular nanoarchitectures utilizing natural polysaccharide as a one-dimensional host

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Abstract We recently revealed that β-1,3-glucans act as unique natural nanotubes, which can accept functional polymers and molecular assemblies in an induced-fit manner. A variety of individual conjugated polymers or molecular assemblies can be incorporated into the one-dimensional hollow constructed by the helical superstructure of β-1,3-glucans to create water-soluble one-dimensional nanocomposites. The advantageous point of the present hosting system is that the selective modification of β-1,3-glucans leads to the creation of various functional one-dimensional nanocomposites in a supramolecular manner. Furthermore, the composites with functional surfaces can act as one-dimensional building blocks toward further hierarchical self-assembles, leading to the creation of two- or three-dimensional nanoarchitectures, which are applicable for fundamental nanomaterials.

Keywords Polysaccharide · Helical polymer · Inclusion complex · Self-assemble · Nanomaterials

Introduction

Recently, the greatest growth has been achieved in the structured determination of natural polysaccharides, and hence increased our understanding related to structural features of natural polysaccharides [1]. The basic

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knowledge of the structural feature of polysaccharides that have helical structure, is essential toward the application as functional polymers including a huge one-dimensional host. For example, X-ray diffraction patterns of various natural polysaccharides have revealed that some of them adopt well-defined helical nanoarchitectures, which never be produced through an artificial polymerization reaction of synthetic molecules, encouraging us to pursue the possibilities as a natural nanotube.

The structural diversity of the natural polysaccharide is fully commensurate with a diverse array of molecules that can be generated from only a limited number of monosaccharides as building blocks by linking them in a variety of ways. This structural feature of polysaccharide characterized by diversity is in sharp contrast to that of other natural polymers such as polynucleotides and proteins with very regular, uniform and well-identified nanostructures.

Amylose is a most familiar polysaccharide with regular helical structures defined at the nanoscale (Fig. 1a). This structural feature of amylose can be regarded as one of the typical helical nanotube, and actually amylose forms the well-known "blue complex" with iodine [2, 3]. Based on the fundamental hosting ability of amylose, so far, several research groups have independently demonstrated that amylose can entrap various functional molecules or polymers, acting as a one-dimensional natural host. For example, Kim et al. have reported that hydrophobic cyanine dyes with alkyl tails are entrapped into the helical cavity to give water-soluble complexes [4, 5]. Sanji and Tanaka reported that partially carboxymethylated amylose (CMA) can entrap the oligosilane in the helical cavity to give insulated wire-like architectures [6, 7]. Partially 2,3-*O*-methylated amylose (MA) also exhibits the excellent hosting ability toward polymer guests such as poly(tetrahydrofuran) and poly(ε-caprolacton) as reported by Akashi

et al. [8]. The helix content of MAs, which is regarded as a measure of the helix-forming ability, could be tuned by the methylation ratios. Consequently, MAs with the moderate methylation ratio tend to form stable inclusion complexes with the selected guest polymers. As an alternative strategy toward the formation of inclusion complexes using amylose host, Kadokawa et al., have demonstrated that the enzymatic polymerization of glucose occurs on the template polymer, where phosphorylase catalyzes a polymerization reaction of α-D-glucose 1-phosphate monomer along the template polymer (poly(tetrahydrofuran)) in the twisting manner [9]. Accordingly, this strategy can be an alternative way to give insulated wire-like architectures.

Cyclodextrines (CDs) are known to form inclusion complexes with various low-molecular weight compounds (Fig. 1b) [10]. Therefore, CDs have ideal structures for the construction of molecular nanotubes [11–14]. Harada et al. have successfully demonstrated that a series of CDs are threaded onto a polymer chain to give pseudo-polyrotaxane structures [15–20]. Although the resultant CDs array structure may not be "true" nanotube, the cross-linking of the adjacent CDs on a template polymer leads to the creation of the complete tubular structures constructed by CDs even after removing the template polymer. In the light of nanotube structure, the CD nanotubes have rigid and closed ring structure, whereas polysaccharide hosts have somewhat flexible one-dimensional cavity arising from helical structure.

β-1,3-Glucans as potential one-dimensional host

β-1,3-Glucans are present in a number of fungi, where their functions as a structural polysaccharide like cellulose, e.g., extracellular microbial polysaccharide and they are essentially a linear polymer of $(1 \rightarrow 3)$ linked β-D-glucose units (Fig. 1c, d) [21–27]. Among a series of β-1,3-glucans, curdlan (CUR) is known as one of the simplest β-1,3-glucan [28–33]. X-ray diffraction patterns of CUR in the anhydrous form revealed that it adopts a right handed 6_1 triple helix with diameter of 2.6 nm and pitch of 1.8 nm (Fig. 2) [21]. In contrast to the simple CUR structure, schizophyllan (SPG) has side glucose groups linked at every third main-chain glucoses. The side glucose groups endow SPG with the water-solubility, whereas they do not affect the helical conformation of the main-chain. Interestingly, the helical parameters of β-1,3-glucans are almost consistent with those of double-stranded DNAs. On the basis of this fact, Sakurai et al. have reported the first example that β-1,3-glucacn could form a complex with some polynucleotides [34, 35]. These intriguing findings encouraged us to apply this unique and unusual hosting system to other functional polymeric guests, where the denature and renature processes of β-1,3-glucans play a significant role in inclusion of various functional materials, such as polymers, molecular assemblies, inorganic particles, etc.

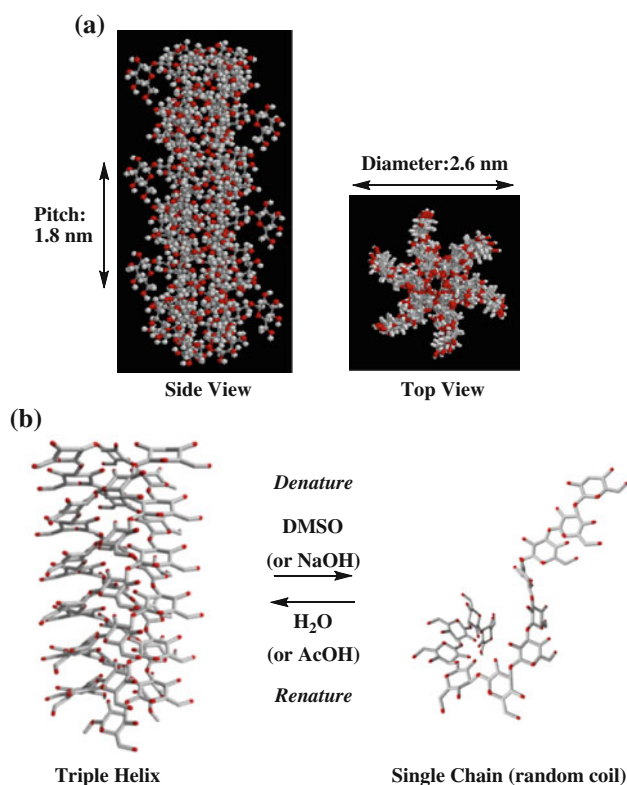Fig. 1 Repeating units of amylose, α-cyclodextrin, and β-1,3-glucans (SPG and CUR)

(a) Amylose

(b) α-Cyclodextrin

(c) Schizophyllan (SPG)

(d) Curdlan (CUR)
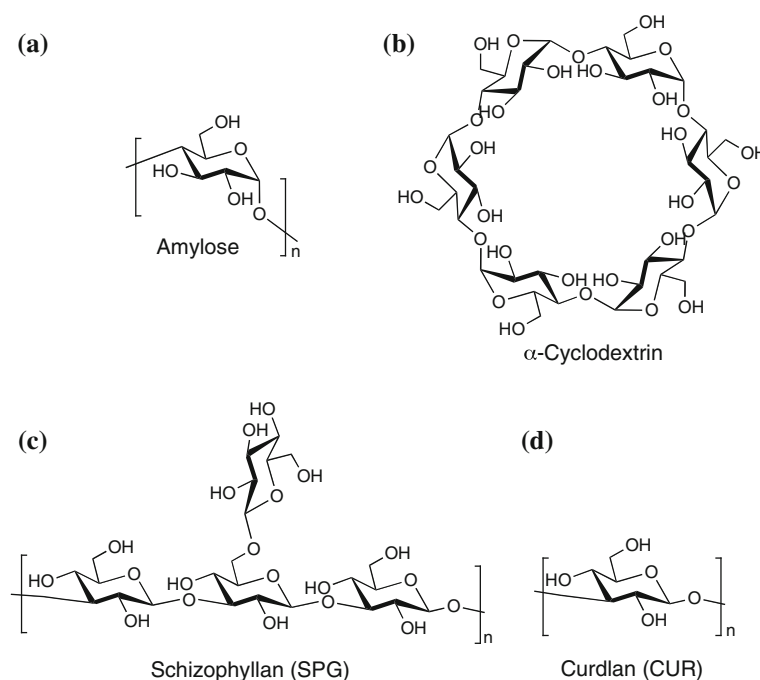
Fig. 2 Calculated SPG triple helix structures based on crystal structure of CUR (**a**), and schematic illustration of denature/renature processes (**b**)

Chemically modified β-1,3-glucans:synthetic strategies toward the selective modification

Many polysaccharide researches have focused on exploiting the functional material thorough chemical modification of polysaccharides, especially for most abundant polysaccharides, amylose and celloses. Chemical modification of β-1,3-glucans has also been independently developed by several research groups including us [28–33, 36–46]. Here, to prepare the functionalized β-1,3-glucan one-dimensional hosts, the selective modification targeting to side-glucoses for SPG and 6-OH groups for CUR need to be exploited, because 2- or 4-OH groups connected to the main-chain glucose units are indispensable for the construction of the inherent helical structure [1]. Based on this fact, we have successfully established a versatile synthetic route to introduce various functional groups selectively into the side-glucoses of SPG and 6-OH groups of CUR, without affecting the inherent helix-forming properties of β-1,3-glucans (Schemes 1, 2). Since the functional groups, introduced into the side-glucoses of SPG or 6-OH groups of CUR, always exist on the surface of the helical structures, the resultant polysaccharide would act as a

functionalized sheath for synthetic polymers as well as molecules.

CUR has one primary OH group in its repeating unit, appending at C-6, i.e., 6-OH group, which would be an active nucleophile under appropriate reaction conditions, making the selective modification of 6-OH groups possible. Moreover, the quantitative reaction can be achieved through the azideation reaction of 6-OH, followed by "click reaction", which involves a Cu(I)-catalyzed chemoselective coupling between organic azides and terminal alkynes [37, 38]. This newly exploited strategy allows us to directly introduce various functional groups into 6-OH groups of CUR (Scheme 1). Actually, we have successfully developed that 6-OH groups of CUR are convertible to various functional groups, e.g., ferrocene, pyrene, phorphyrin, trimethylammonium, slufonate, etc., and found that these functional groups in the side chains govern the chemical properties of the modified CUR. The advantageous point of this method is that a series of reaction proceed quantitatively and selectively. Additionally, by adjusting the feed acetylene composites, different functional groups are easily introduced into the same CUR chain in a step-wise manner.

SPG has two primary OH groups on the main chain and side glucose groups, so that the selective modification targeting to the primary OH groups seems to be difficult. On the other hand, the side glucose groups of SPG have 1,2-diols (cis-diols) at 2-OH, 3-OH and 4-OH positions, whereas main chain glucoses have no such a diol structure. Therefore, oxidative cleavage by $NaIO_4^-$, which is known as a selective oxidation reaction at 1,2-diols structure, would proceed selectively only at the side glucose units of SPG. Combining this oxidative cleavage reaction with the reductive amination reaction, these classical synthetic strategies can be a powerful tool for the selective modification of the native SPG chain (Scheme 2). Actually, we have demonstrated that a series of chemically modified SPGs bearing various molecular recognition moieties, e.g., ionic groups, saccharide, amino acid, co-enzyme, etc., can be successfully obtained according to this synthetic strategy [39–43]. Here, it should be important to address the discrepancy between the chemically modified CURs and SPGs obtained through the synthetic route described above: 6-OH groups of CUR can be converted to functional groups "quantitatively", whereas the side glucose groups of SPG can be "partially" functionalized because excessive oxidation of the side glucoses causes the insoluble aggregate probably due to the interpolymer cross-linking between 6-OH and aldehyde groups thus formed. The modification percentage of the side glucose groups is, at most, 30%.
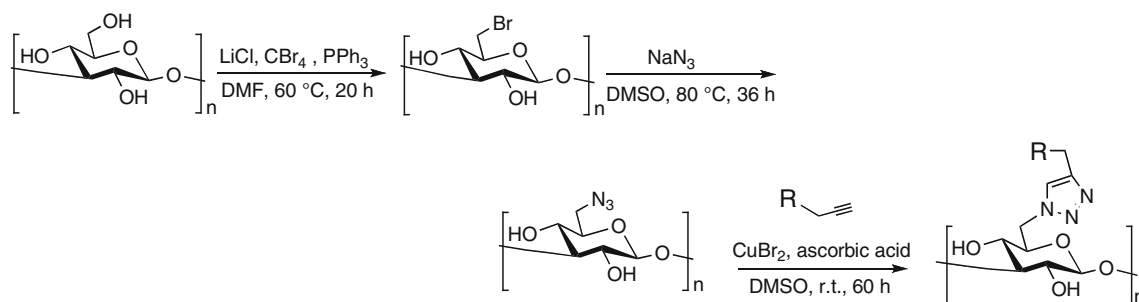
Scheme 1 Chemical modification of COR
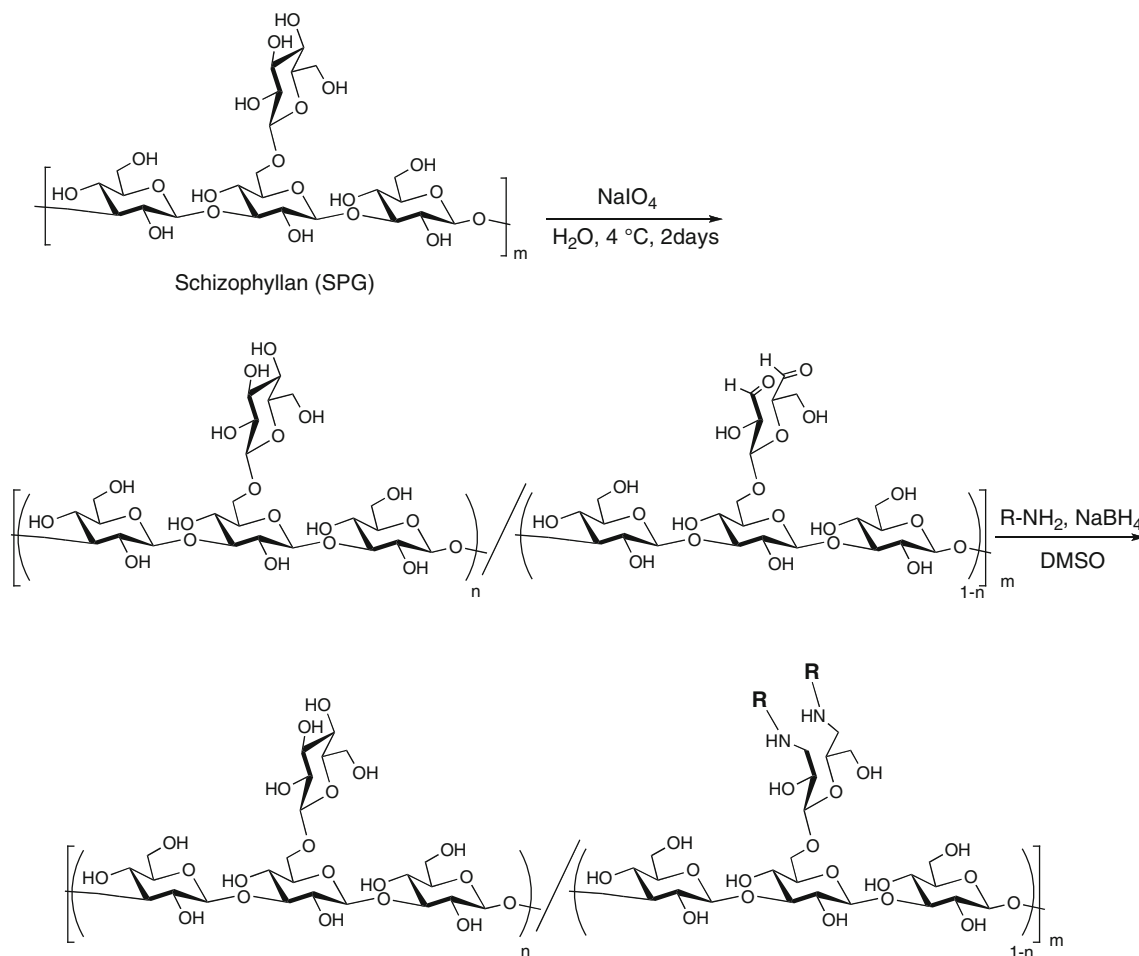
Scheme 2 Chemical modification of SPG

Unique one-dimensional hosting abilities:inclusion of single-walled carbon nanotube (SWNT)

Since the discovery of single-walled carbon nanotubes (SWNTs) by Iijima, they have been regarded as ideal nanomaterials due to their unique electronic, photochemical and mechanical properties [47, 48]. Much effort has been paid to apply SWNTs as practical nanomaterials, however the strong cohesive nature and poor solubility of

SWNTs have caused the serious problem; that is, these properties still hamper for researchers to handle SWNTs as "functional polymers". As a potential solution to overcome this problem, it would be worth to wrap SWNTs by synthetic or biological polymers, promoting the dissociation of SWNTs bundle to give homogeneous solution without damaging SWNT surfaces [49–55]. In particular, natural polysaccharide such as amylose is an excellent solubilizer for SWNTs, because polysaccharides have no light

absorption in the UV–VIS wavelength region, being suitable for exploiting the photochemical properties of the resultant composite. The first example is SWNTs/amylose composite formation reported independently by Kim et al. and by Stoddard et al. [56, 57]. It was shown therein that SWNTs can be incorporated into the amylose cavity to form the water-soluble inclusion complexes.

The main driving force for the reconstruction of the triple-stranded β-1,3-glucans from the single-stranded ones are considered to be the hydrophobic interaction in addition to the hydrogen-bonding interactions. It is expected, therefore, that SWNTs might be entrapped in the inside hollow of the β-1,3-glucans helical structure mainly owing to the hydrophobic interaction (Fig. 3). Unlike the amylose hosting system, however, natural β-1,3-glucans have no enough cavity to accommodate SWNT with 1–2 nm diameters. Thus, some conformational change in β-1,3-
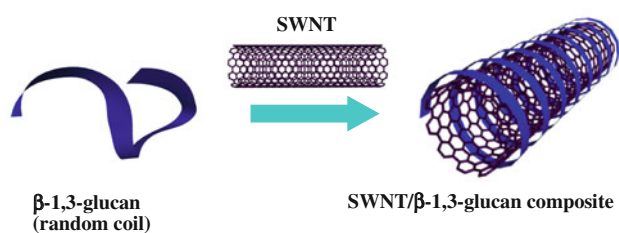

Fig. 3 Schematic illustration of the formation of SWNTs/β-1,3-glucan composite

glucan main-chain would be needed after entrapping the guest polymers.

As a preliminary experiment to investigate whether β-1,3-glucans can actually entrap such a rigid polymer into their cavities, SWNTs were cut into an appropriate length (1–2 μm) by the acid treatment, which makes handling of SWNTs easy [58]. As a result, the cut SWNTs (c-SWNTs) can be easily dispersed into water, but they still tend to form bundle structures with several tens nanometer in diameters. Consequently, an s-SPG (M_w = 150 KDa) DMSO solution was directly added to an aqueous solution containing the bundle c-SWNTs, according to the same procedure as the case of polynucleotide guests, expecting that SWNTs are entrapped into the SPG cavity. To remove an excess amount of SPG feed, the resultant solution was subjected to centrifugations. The presence of c-SWNT in the obtained aqueous solution was evidenced by the measurements of VIS–NIR and Raman spectroscopy. The direct evidence that SWNTs are really entrapped into the SPG cavity was confirmed by Atomic Force Microscopy (AFM). Interestingly, the surface of the obtained composite showed a periodical structure with inclined stripes, reflecting the strong helix-forming nature of the β-1,3-glucan main-chain (Fig. 4). The periodical interval in the helical stripes was estimated by AFM. It was confirmed from scanning along a fibril that the periodical pattern appears at every 16 nm intervals. In addition, from the height profile analysis by AFM, it was revealed that most

Fig. 4 AFM images of **a** c-SWNTs, **b** c-SWNTs/SPG composite, **c** c-SWNTs/CUR composite, **d** magnified picture of fibrils in s-SWNTs/SPG composite. Amorphous structure observed around the composite is considered to be uncomplexed CUR which cannot be removed during centrifugation process due to its poor solubility in water
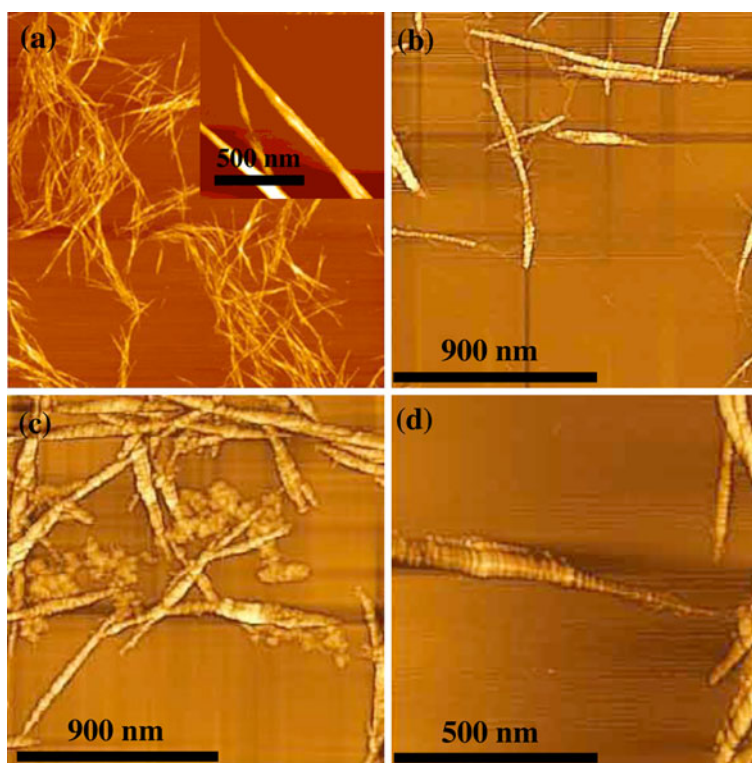
composites have ca. 10 nm in height, indicating that β-1,3-glucans can wrap around bundle c-SWNTs, with changing their original helix parameters. As a reference experiment, on the other hand, when a DMSO solution of s-SPG was cast on mica, we could observe a fine polymeric network structure. Besides, the surface of c-SWNTs themselves did not give any specific patterns as seen in the composite surface. These results clearly show that β-1,3-glucan can act as a one-dimensional host for SWNTs, where the characteristic helical structure of β-1,3-glucans is reconstructed on the SWNTs surface [59]. The β-1,3-glucan one-dimensional host is characterized by this well-identified wrapping mode arising from the strong helix-forming nature of β-1,3-glucans; that is, the hydrophobic inner surface of β-1,3-glucans interact with SWNTs, whereas the hydrophilic surface exist on the composite surface. It should be noted that only the composites containing bundle SWNTs are intentionally highlighted for the microscopic observation because the helical structure constructed on such a composite can be easily recognized by the microscopic techniques.

Natural CUR is scarcely soluble in water due to the lack of side glucoses. Nevertheless, when CUR chain was cut into a moderate length, e.g., several tens thousand, by formic acid-hydrolyzed treatment [60], the resultant CUR acts as a one-dimensional host like SPG. Actually, when s-CUR was used as a wrapping agent instead of s-SPG, the similar periodical structure as seen in c-SWNT/SPG composite can be observed on bundled SWNTs. As reference experiments to characterize the wrapping property of β-1,3-glucans, we performed the same experiments with amylose, dextran, and pulluran as polysaccharide hosts, but none of them could disperse ag-SWNTs into water. The findings lead to the conclusion that the $\beta(1 \rightarrow 3)$ glucose linkages are indispensable for the unique hosting capabilities.

On the basis of the preliminary experiment using c-SWNT as a guest polymer, we intend to apply the present wrapping system to as-grown SWNTs (ag-SWNTs), which are favorable for practical nanomaterials because of no electrochemical defect on the SWNT surface. Although, unlike c-SWNTs, ag-SWNTs have strong tendency to form bundle structure, they are easily dispersed into water after entrapping into the β-1,3-glucan cavity with the aid of sonication. This remarkable solubilization capability of SPG even for ag-SWNTs allows us to investigate the detailed properties of the resultant ag-SWNTs/SPG composites [61]. Firstly, the composite was subjected to VIS–NIR measurements in D_2O solvent (Fig. 5). The characteristic sharp bands, which are assignable to individual SWNTs, can be observed in VIS–NIR region, supporting the view that one or a few pieces of ag-SWNTs are included in the SPG helical structure. AFM observations support the view more quantitatively. From the height profile of the composite, it can be recognized that most of them have 2–3 nm in diameter and
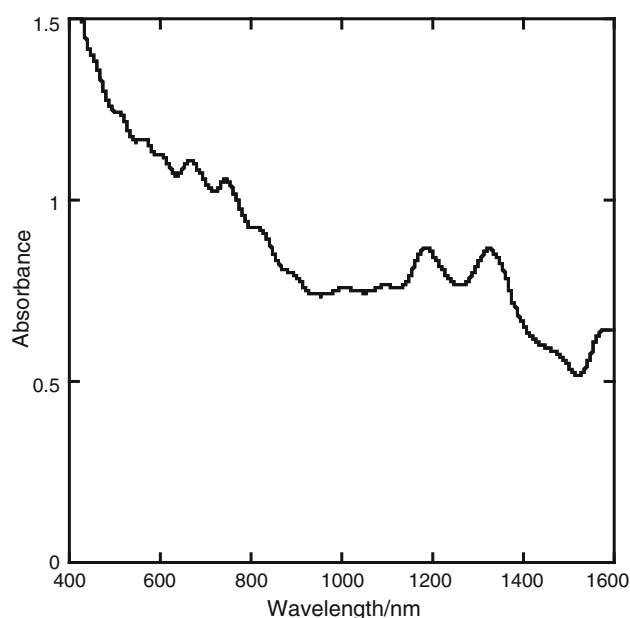

Fig. 5 VIS-NIR spectrum of ag-SWNTs/SPG solution: D_2O, cell length 1.0 cm, room temperature. Reprinted with permission from Ref. [61]

the distribution is very narrow. Furthermore, when the surface of the composite was scanned along the fibril, a periodical pattern as seen in c-SWNT/SPG composite can be recognized. Subsequently, the ag-SWNTs/SPG composite was directly characterized by high-resolution TEM (HRTEM). Two s-SPG chains twine around one ag-SWNT are clearly recognized in the Fourier filtered image as shown in Fig. 6, providing "decisive" evidence that one piece of ag-SWNTs is wrapped by s-SPG chains. The helical pitch is estimated to be ca. 10 nm, which is longer than that of the original triple helix, suggesting the view that the conformation of SPG chains is changeable with incorporating ag-SWNTs. The conformational changes in the main-chain of β-1,3-glucans would be allowed only to single- or double-stranded helix because the main chains in the triple-stranded helix tightly interact with each other.

If β-1,3-glucans maintain their characteristic helix-forming nature even on the SWNT surface, the dissociation from SWNTs would be promoted by addition of DMSO or NaOH, in which β-1,3-glucans exist as a single chain. As shown in Fig. 7, when DMSO was added to the aqueous solution containing the composite adjusting the final composition to be 50 v/v %, the entrapped ag-SWNTs were immediately precipitated out. This result gives the strong impression that the composites are stabilized by non-covalent interactions occurring between the hydrophobic core and the hydrophilic shell, which can be easily peeled off by the various chemical stimuli.

As a summary of the forgoing findings, particularly interesting are the facts that β-1,3-glucans have potential
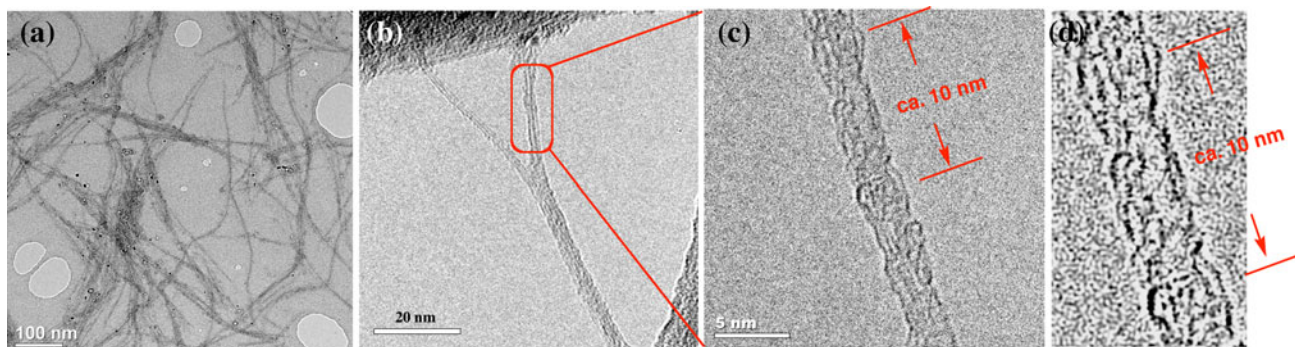
Fig. 6 **a** TEM image of ag-SWNT/SPG composite, and **b**, **c** its magnified picture. **d** The original image of (**c**) was Fourier filtered to enhance the contrast of the composite. Reprinted with permission from Ref. [61]
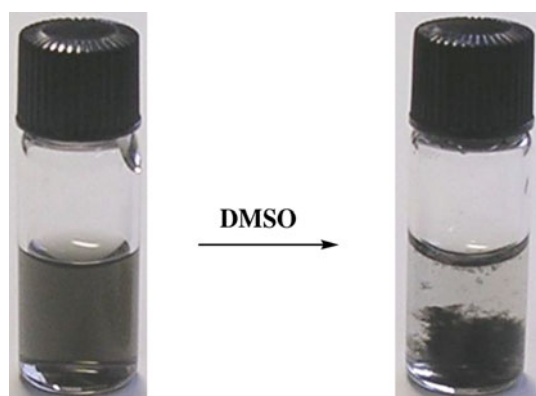

Fig. 7 Picture of aqueous ag-SWNTs/SPG composite solution (*left*) and that taken after addition of DMSO (*right*): the final solution contains 50 v/v % DMSO. Addition of aqueous 1.0 M NaOH solution results in the similar precipitate of ag-SWNTs. Reprinted with permission from Ref. [61]

abilities to accommodate rigid and hydrophobic guest polymers such as SWNTs, the structural feature of which is totally different from polynucleotides with somewhat flexible helical structures. The finding obtained from the novel composite leads to the conclusion that β-1,3-glucans can act as a one-dimensional host for various hydrophobic polymers in an induced-fit manner without being affected by the diameter as well as the chemical properties of the guest polymers.

Chemical modification of SPG: supramolecular functionalization of guest polymers through wrapping with chemically modified polysaccharide hosts

When polymeric guests or molecules are entrapped into the SPG cavity, the side group glucose should exist on the surface of the composites. If this is the case, a functional group introduced into the side group glucose would be useful as a recognition target. To test this idea, lactose-modified SPG (SPG-Lac) was synthesized according to

Scheme 2, and used it as a wrapping reagent for c-SWNTs. Molecular recognition event of the obtained c-SWNTs/SPG-Lac composite was assessed by surface plasmon resonance (SPR) using lectin-immobilized Au-surfaces [42]. In the case of c-SWNTs themselves, the increment of the resonance-unit is observed for all lectin-immobilized surfaces, indicating that non-specific binding occur on c-SWNT surface. Since detergent-containing buffer solution could release the c-SWNTs from the lectin-immobilized surfaces, this non-specific binding can be ascribed to hydrophobic interactions between c-SWNT and lectin. On the other hand, in the case of c-SWNTs/SPG composite, no or negligible binding can be observed for all lectins, demonstrating that the hydrophobic nature of SWNTs is effectively shielded by the wrapping effect. The most fascinating data were obtained from c-SWNTs/SPG-Lac composite, where the specific binding is observed for the Au-surface immobilized with ricinus communis agglutinin (RCA120, β-Lac-specific). In contrast, the other lectin-immobilized surfaces showed negligible resonance changes, clearly demonstrating that the affinity of c-SWNTs/SPG-Lac composite is highly specific toward RCA120. These results clearly indicate that chemically modified SPG can act as a one-dimensional host for c-SWNTs and the surface properties of the obtained composite are totally governed by the functional groups introduced into the side glucose groups.

PANI is one of the most promising and widely studied conductive polymers owing to its high chemical stability, high conductivity and unique redox properties [62–64]. In spite of these advantages, PANI and its derivatives are hardly applicable for conductive nanowires in a bottom-up manner, because these PANIs tend to form amorphous aggregates composed of highly entangled polymeric strands. Much research effort has been therefore paid for manipulation of an individual PANI nanofiber and for fabrication toward parallelly-aligned strands to show excellent conductivity through the nanofibers.

From the forgoing c-SWNTs/SPG composite system, it is expected that β-1,3-glucans can fabricate PANIs nanofiber structures with several tens nanometer in diameter, acting as a one-dimensional host for PANIs bundles. TEM images as showed in Fig. 8 reveal that the wrapping of PANIs by SPG results in the formation of fibrous architectures. The observed nanofibers are highly contrasted without any staining due to the adsorption of the electron beam. The lengths of the contrasted fibers were consistent with that of used SPG. Importantly, the contrast, which should arise from incorporated PANIs, continuously exists all over the range of the obtained composite. Since the length of used PANIs is rather shorter than that of s-SPG, the incorporated PANIs fibers are bundled into the one-dimensional fibers along the SPG cavity. The diameter of the smallest fiber is estimated to be around 10 nm, indicating that the several PANI strands are co-entrapped within the one-dimensional cavity.

To fabricate the surface functionality of the obtained PANIs/SPG composites in a supramolecular manner, mannose-modified SPG was synthesized according to the reported procedure and used it as a wrapping reagent for PANIs [65]. The specific interaction between the composite and ConA was estimated by a CLSM using a FITC-labeled ConA (Fig. 9). The CLSM observation clearly shows that PANIs and ConA coexist in the same domain, indicating that (1) mannose-modified SPG can also wrap PANIs and (2) the mannose groups introduced into the side groups would exist on the exterior surface of the composite. These findings clearly show that chemically modified SPG maintains its inherent ability as a one-dimensional host. The wrapping of the chemically modified SPG provides a novel strategy to create functional polymer composites in a supramolecular manner. Considering a general difficulty in introducing functional groups into the functional polymer backbones, the present system can be a new potential path to develop functional polymeric materials.

From the forgoing findings, one of the most attractive aspect of β-1,3-glucans is that they have potential abilities to accommodate various guest polymers due to their flexible conformational changes, without being affected by the diameter as well as the chemical properties of guest polymers. Additionally, once we synthesize a series of modified β-1,3-glucans, functionalization of the polymer guests can be easily achieved through the supramolecular wrapping of the modified β-1,3-glucans. To show the further ability of β-1,3-glucans as a versatile functional host, we have extended the present one-dimensional hosting systems toward other conjugated polymers.

π-Conjugated polymer guests: inclusion of poly(thiophene) (PT) and poly(p-phenyleneethynylene) (PPE)

So far, several intriguing approaches have been developed to fabricate an individual PT fiber, including covalent and non-covalent approach in which the PT backbone is shielded by wrapping within a dendritic wedge or threading PT through CDs sheath [66–70]. Here, we intended to prepare a well-ordered stoichiometric one-dimensional nanocomposites, such as polynucleotide/β-1,3-glucan complexes, in which only one piece of polymer is incorporated into the helical cavity constructed by two β-1,3-glucans. Along this line, in the present study, water-soluble cationic polythiophene (PT–N$^+$) was synthesized, because the water-solubility of PT–N$^+$ arising from the polycationic nature would result in a well-characterized PT–N$^+$/β-1,3-glucan composite, in which stoichiometric interaction between PT–N$^+$ and β-1,3-glucan can be achieved (Fig. 10). Figures 11a, b show absorption and emission spectra, comparing between PT–N$^+$ and PT–N$^+$/SPG composite. The absorption maximum of PT–N$^+$ appears at 403 nm, whereas that of PT–N$^+$/ SPG composite is drastically red-shifted to 454 nm by ca.

Fig. 8 **a** TEM images of PANIs/SPG composites, **b** magnified image of (**a**), the images were taken without staining. PANIs themselves afforded spherical massive aggregates. Reprinted with permission from Ref. [65]
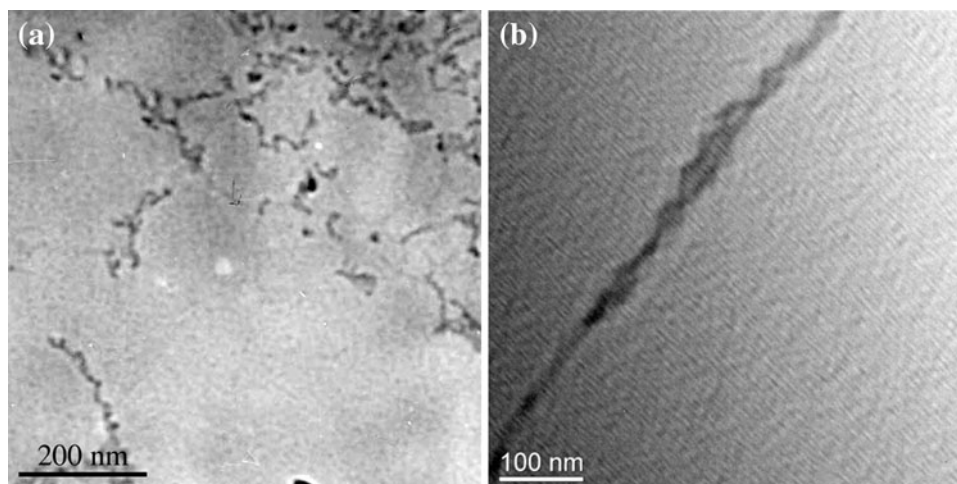
Fig. 9 a Concept of the supramoleuclar functionalization of the entrapped guest polymers. CLSM images of PANIs/mannose-modified SPG composite + FITC-ConA, **b** fluorescence image, **c** optical microscope image, **d** overlap of (**b**) and (**c**). Reprinted with permission from Ref. [65]
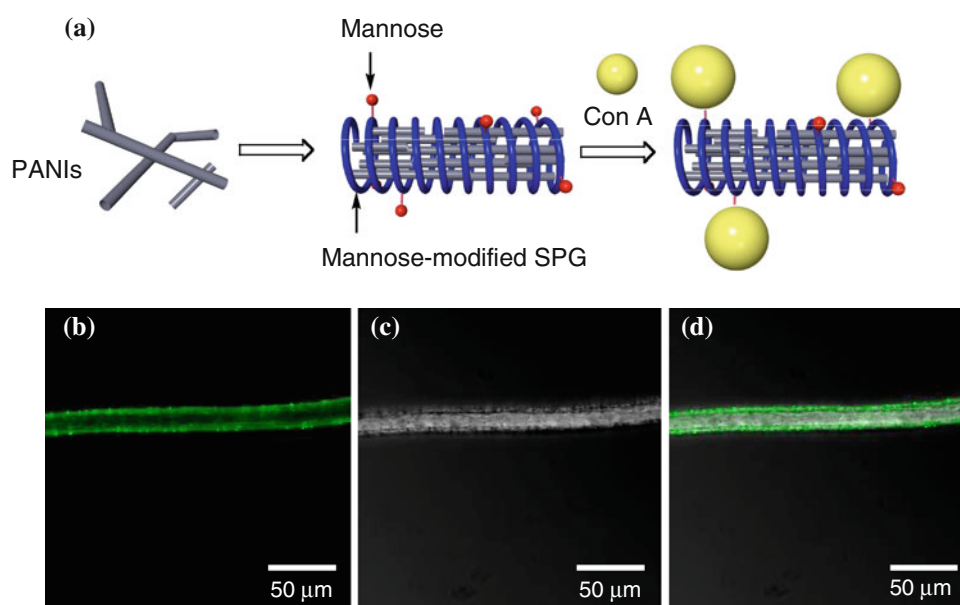
Fig. 10 Schematic illustration of the chirally insulated PT–N$^+$ in the helical SPG cavity
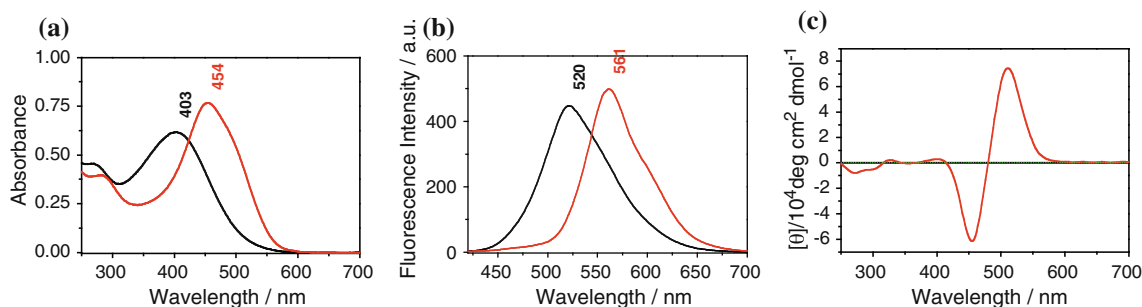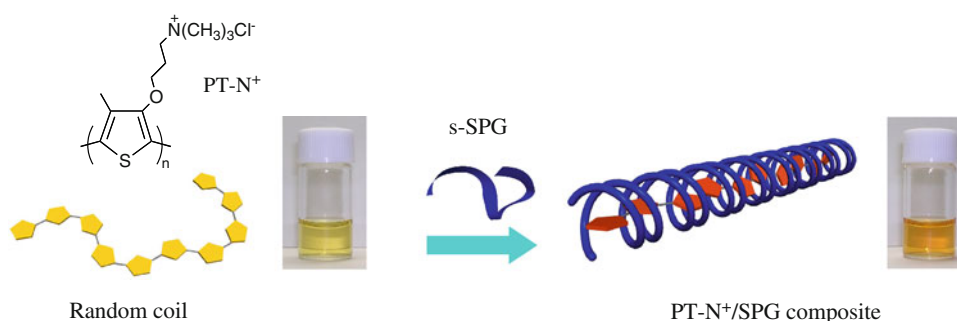
Fig. 11 a UV–VIS, **b** emission ($\lambda_{ex} = 400$ nm), and CD spectra of PT–N$^+$: the spectra were taken without SPG (*black line*) and with SPG (*red line*) (Color figure online)

50 nm, demonstrating that SPG forces the PT backbone to adopt a more planar conformation with increasing the effective conjugation length. In general case, when PTs form π-stacked aggregates in poor solvent, the UV–VIS spectrum is characterized by the appearance of vibronic band in the longer wavelength region [71]. In the present system, however, such a peak attributable to the stacked aggregate was not observed.

The emission maximum (561 nm) of PT–N$^+$/SPG composites is also red-shifted from that of free PT–N$^+$ (520 nm) and slightly increases in the intensity, supporting the view that the PT–N$^+$ backbones become more planar and more isolated in the SPG cavity. It should be emphasized that no red shift of the absorption peaks is observed for the cast films of PT–N$^+$/SPG composite, indicating that the PT–N$^+$ backbone is shielded by the SPG sheath, by which unfavorable interpolymer stacking of the PT–N$^+$ backbone is strongly restricted even in the film.

The CD spectra of the composites show an intense split-type ICD in the π–π* transition region (Fig. 11c). This fact

clearly suggests that PT–N$^+$ would be chirally twisted in an intrastranded manner. The observed ICD patterns are characteristic of a right-handed helix of the PT backbones, reflecting the right-handed helical structure of SPG [72]. The stoichiometry of the composite was determined by means of continuous-variation plots (Job plots) from the CD spectra (Fig. 12). Consequently, the molar ratio of glucose residues along the main chain to the repeating unit of PT–N$^+$ can be determined to around 2. The complexation mode of PT–N$^+$/SPG composite is almost same as that of polynucleotide/SPG complex. This fact leads to the conclusion that SPG tends to form hetero-macromolecular complexes by exchanging one glucan chain in t-SPG for one water-soluble guest polymer.

Along this line, to show the inherent nature of β-1,3-glucans for the formation of hetero-macromolecular complexes, water-soluble PPE (poly (p-phenylene ethynylene)) was selected as a guest polymer for β-1,3-glucan hosts. PPE is also a conjugated polymer which has been regarded as a suitable probes for chemosensors due to its excellent optical response to environmental variation through the relatively free rotation of the alkenyl-aryl single bond [73–80]. A particularly challenging aspect of PPE is to design a water-soluble PPE backbone with a one-handed helical structure because it is readily applicable as a sensitive chiral sensor targeting to biologically important molecules and polymers. As a novel approach toward the creation of a chiral insulated PPE wire, β-1,3-glucans should exert their unique hosting abilities [81].

Taking the result obtained from PT–N$^+$/SPG system into consideration, water-soluble PPE (PPE–SO$_3^-$) was used in the present study. Figure 13a compares the absorption spectra between PPE–SO$_3^-$ itself and its mixture with s-SPG. The absorption maximum of 442 nm observed in the absence of SPG is attributed to a random-coiled conformation of the PPE backbone. Upon mixing with s-SPG, however, the absorption maximum is red-shifted to 470 nm and the solution color changed from yellow to orange. The fact suggests that the effective conjugation length of the PPE backbone is increased in the SPG cavity, where s-SPG would force the PPE backbone to adopt planer and rigid conformation. Furthermore, fluorescence spectra of the PPE–SO$_3^-$/SPG composite revealed that the emission intensity dramatically increases upon addition of s-SPG (Fig. 13b). The finding indicates that the PPE backbones do not aggregate by themselves but become more isolated through the complexation with s-SPG, supporting the view that PPE backbone is insulated into the one-dimensional SPG cavity.

CD spectroscopic studies are also helpful to investigate the conformational changes of incorporated PPE–SO$_3^-$. The shape and ICD pattern of the composite suggest that PPE–SO$_3^-$ would adopt a right-handed helix which is transcribed from SPG to the PPE backbone (Fig. 14). These results are almost consistent with those observed for the PT–N$^+$/SPG system, encouraging us to pursue the fundamental properties of SPG as a one-dimensional host.

The stoichiometry of the PPE–SO$_3^-$/SPG composite was determined by means of a continuous-variation plot (Job plot) from its CD spectroscopic change. From the Job plot, the maximum complex formation is attained at around 2, which corresponds to the molar ratio of the glucose residue along the s-SPG main chain to the repeating unit of PPE–SO$_3^-$. Considering the facts that t-SPG forms a right-handed 6$_1$ triple helix with a 1.8 nm pitch and that three p-phenylene ethynylene units have statistically 1.6 nm length in average, we suppose that the PPE–SO$_3^-$/SPG composite is constructed by two s-SPG chains and one PPE–SO$_3^-$ chain. Together with the results obtained from polynucleotide/SPG and PT/SPG composites, it can be concluded that when s-SPG interacts with relatively hydrophilic guest polymers, the resultant composites are always composed of two SPG polymers and one guest polymer.

σ-Conjugated polymer guest:inclusion of permethyldecasilane (PMDS)

As another type of conjugated polymer guest, we selected poly(silane)s, which have been investigated as attractive functional materials, since they have unique σ-conjugated helical structures and show unique optoelectric properties [82–84]. We have demonstrated that permethyldecasilane is incorporated into the SPG cavity through our successful procedure to a one-dimensional composite [85]. Several lines of evidence including UV–VIS, CD and fluorescence spectroscopic data along with observations using a TEM and AFM have clearly revealed that water-soluble,
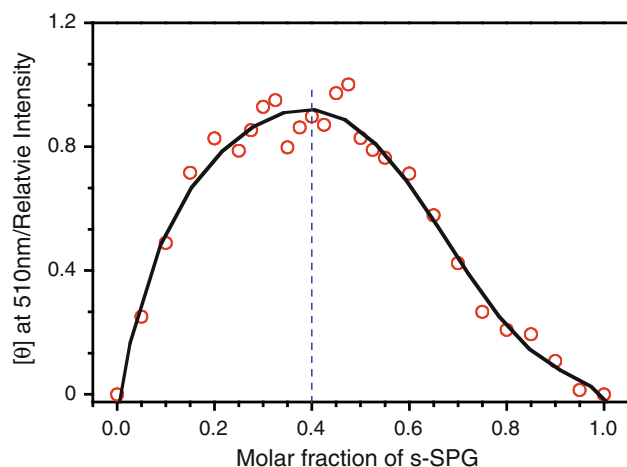
Fig. 12 Job Plot obtained from the CD spectra of PT–N$^+$/SPG composite
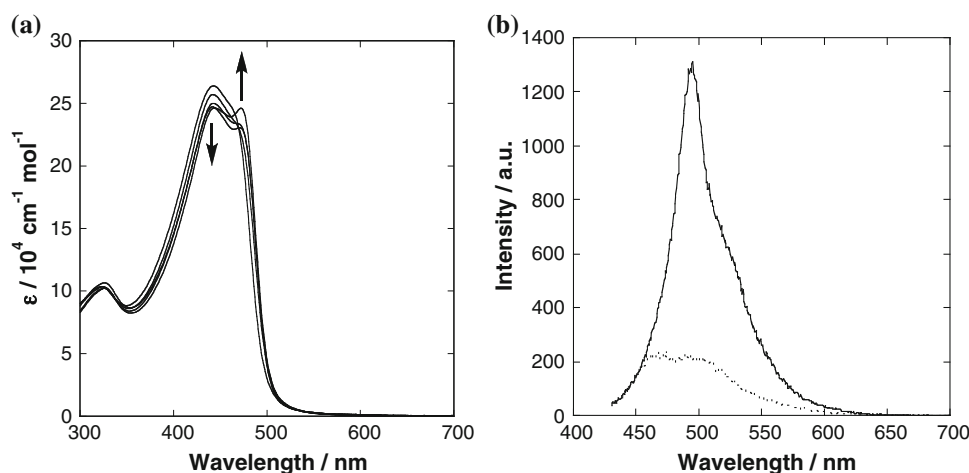
(a)

(b)

Fig. 13 **a** UV–VIS spectral change of PPE–SO$_3^-$ as a function of SPG concentration (concentration range of s-SPG : 0–6.7 × 10^{-4} M). The concentration of PPE–SO$_3^-$ was kept at 1.5 × 10^{-4} M. H$_2$O/DMSO = 95/5 (v/v), 1.0 cm cell length, room temperature. **b** Emission spectra of PPE–SO$_3^-$ in the absence of s-SPG (*dashed*

line) and in the presence of 15.0 eq. (2.3 × 10^{-3} M) of s-SPG (*solid line*), λ_{ex} = 400 nm. The concentration of PPE–SO$_3^-$ was kept at 1.5 × 10^{-4} M. H$_2$O/DMSO = 95/5 (v/v), room temperature. Reprinted with permission from Ref. [117]
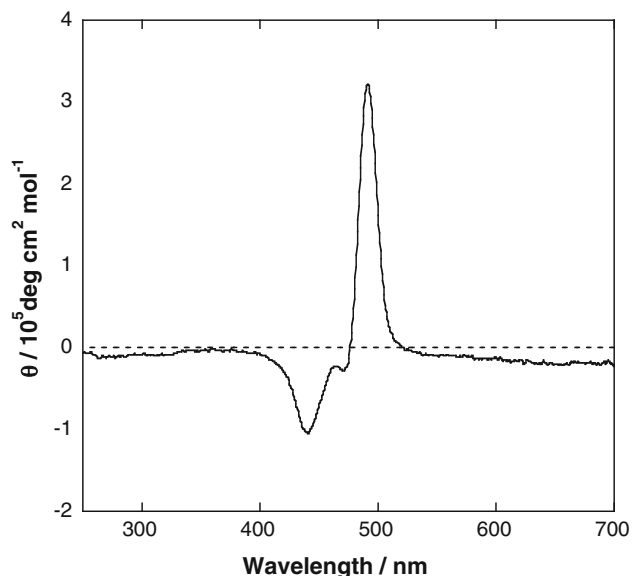

Fig. 14 CD spectra of PPE–SO$_3^-$ in the absence of 15.0 eq. (2.3 × 10^{-3} M) of s-SPG (*dashed line*) and in the presence of PPE–SO$_3^-$ (*solid line*). The concentration of PPE–SO$_3^-$ was kept at 1.5 × 10^{-4} M. H$_2$O/DMSO = 95/5 (v/v), 1.0 cm cell length, room temperature. Reprinted with permission from Ref. [117]

helically ordered oligosilane-nanofibers are formed with s-SPG through the renaturation process.

Unlike the forgoing guest polymers, i.e., SWNT, PANI, PT and PPE, all of which are soluble or dispersible either into water or into polar organic solvents, PMDS is soluble only in nonpolar organic solvents such as hexane. Accordingly, to prepare highly ordered PMDS/SPG composites with excellent reproducibility, establishment of a novel solubilization strategy is desired. A new biphasic

procedure, on the basis of the renaturation process of s-SPG on the liquid/liquid interface, is thus exploited.

The triple strand of SPG is dissociated into the single strand at pH >12, whereas it retrieves the original triple strand by pH neutralization [21]. Accordingly, in the present study, a NaOH solution containing s-SPG was neutralized by acetic acid, where the renaturing from s-SPG to t-SPG proceeds with decreasing pH values. Accordingly, a hexane layer containing PMDS and an aqueous NaOH layer containing s-SPG were well homogenized by sonication to form emulsion. Aqueous acetic acid was then added to the resultant emulsion, where the renaturing from s-SPG to t-SPG would occur on the H$_2$O/hexane interface, resulting in the wrapping of PMDS by SPG. UV–VIS spectrum of the hexane layer showed that characteristic of the σ–σ* transition band of PMDS appear around 280 nm with full-width-half-maximum (FWHM) of 40 nm. Detailed investigation on the concentration dependency of s-SPG indicated that the intensity at 280 nm in the hexane layer was diminished with increasing s-SPG concentration in the aqueous layer. The result indicates that PMDS should be extracted into the aqueous layer with accompanying PMDS/SPG composite formation. The PMDS/SPG composite in neutral aqueous solution showed an intense red-shifted fluorescence band with FWHM of 18 nm at 323 nm when excited at the σ–σ* transition band (280 nm), compared to the corresponding fluorescence band at 310 nm of free PMDS in hexane.

Once the hexane layer was removed by lyophilization of the aqueous layer, followed by re-dissolution of the resultant PMDS/SPG composite into water, the resultant aqueous solution showed a sharp absorption band at 290 nm with a narrow FWHM of 12 nm as well as a positive CD

signal at 283 nm and a negative one at 293 nm (Fig. 15). The small FWHM of this UV band suggests a very rigid, extended conformation of PMDS in the PMDS/SPG [86].

CD spectroscopic study can provide further detail information on helical conformation of the incorporated PMDS chain. The origin of the bisignate CD spectral profile as shown in Fig. 15a indicates two possibilities. One possibility is that a mixture of two different helices with the opposite screw senses and another is that different pitches and exciton couplet due to chirally-twisted PMDS aggregates. Kunn's dissymmetry ratio being defined as $g_{abs} = \Delta\varepsilon/\varepsilon = CD$ (in mdeg)/32980/Abs.), which is a dimensionless parameter to semi-quantitatively characterize helical structures of oligosilanes and other chromophoric chiral molecules, excludes the latter case, because the evaluated g_{abs} values at two extrema are $+3.3 \times 10^{-4}$ at 283 nm and -1.7×10^{-4} at 293 nm, respectively. The absolute magnitude in these small g_{abs} values is almost comparable with the g_{abs} value of $(2.0–2.5) \times 10^{-4}$ at 323 nm of rigid rod-like poly(silane) which has a single-screw helix conformation. PMDS incorporated in the helical cavity of s-SPG, therefore, exists as a mixture of diastereomeric helices with the opposite screw senses; that is, the 283 nm CD signal is responsible for a P-7_3 helix and the 293 nm CD signal is for an M-15_7 helix. Additionally, UV–VIS and CD spectral features of PMDS/SPG composite are very similar to those for the PMDS/γCD composite [15].

Inclusion of supramolecular dye assemblies

So far, creation of well-regulated supramolecular assemblies from a rationally designed dye molecule have attached the wide-spread interest in view of their potential applications for nonlinear optical and photorefractive devices [81, 87–90]. A particularly challenging aspect is to create a wide

variety of supramolecular one-dimensional assemblies by using an appropriate template polymer, reflecting the higher-order structures of the template [91–103]. As the supramolecular dye assemblies can be regarded as a sort of polymer, established the fundamental hosting abilities of β-1,3-glucans would be further extended to the supramolecular fibrous architectures. The idea was tested by using a dipolar dye (azo-dye) having pyridine and carboxylic acid terminals, which has potential self-assembling capabilities through intermolecular interactions in addition to cooperative π–π stacking and dipolar–dipolar interactions [104, 105]. These intermolecular interactions would be governed by the solvent effects surrounding dye molecules. Thus, we employed the different renature solvents, e.g., DMSO or NaOH solution, expecting that the different molecular arrangement of azo-dye molecule would be achieved in the presence of SPG template: in DMSO solution a self-assembling structure of azo-dye would be more dominated by the hydrogen-bonding interaction, whereas in NaOH solution π–π stacking and dipolar–dipolar interactions in addition to hydrophobic interactions would become major driving forces (Fig. 16). When s-SPG was renatured in the presence of DMSO solution of azo-dye, the absorption maximum of the azo-dye/SPG solution thus obtained was red-shifted to 468 nm by 22 nm, compared with azo-dye itself in the same solvent [106]. This red-shift can be ascribed to the formation of J-type assemblies, promoted by the intermolecular hydrogen bonding in addition to π–π stacking interactions among azo-dye molecules. Upon mixing with s-SPG an intense split-type ICD also appeared in the π–π* transition region of azo-dye assembly. The result indicates that the self-assembling nanofiber structure of azo-dye is entrapped into the helical SPG cavity, with adopting twisted molecular arrangement (Fig. 17).

As another strategy, we tried to construct the different-type of azo-dye assemblies utilizing this neutralization

Fig. 15 **a** UV (*bottom*) and CD (*top*) and **b** fluorescence spectra of the PMDS/SPG composite in water ($\lambda_{ex} = 290$ nm, *red solid line*), the PMDS/t-SPG mixture in water ($\lambda_{ex} = 290$ nm, *blue solid line*) and free PMDS in hexane ($\lambda_{ex} = 280$ nm, *black dotted line*): (s-SPG)/(PDMS) = 1.2 in molar ratio, cell length 0.5 cm and 25 °C. Reprinted with permission from Ref. [85] (Color figure online)
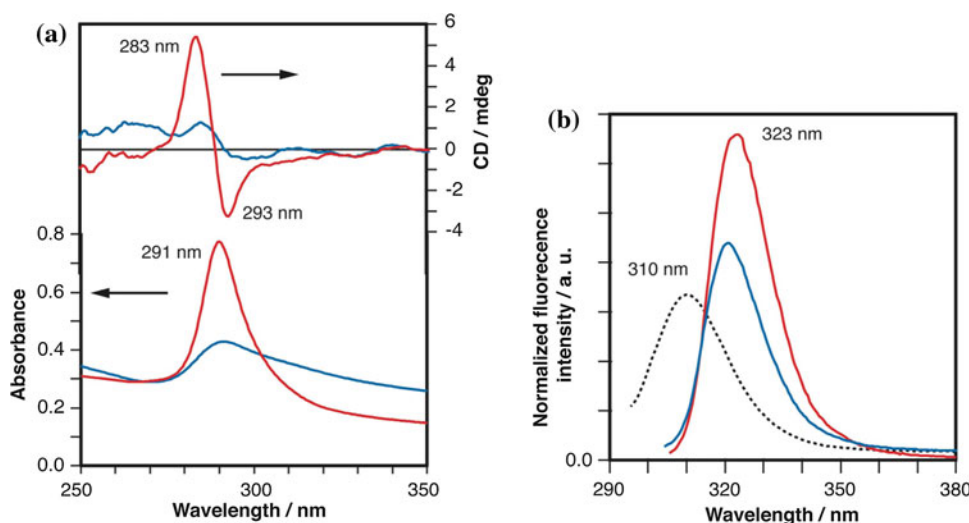
Fig. 16 Concept of the creation of supramoleculer dye architectures showing "polymorphism". Structure of the designed dipolar dye with pyridine and carboxylic acid terminals. Reprinted with permission from Ref. [106]
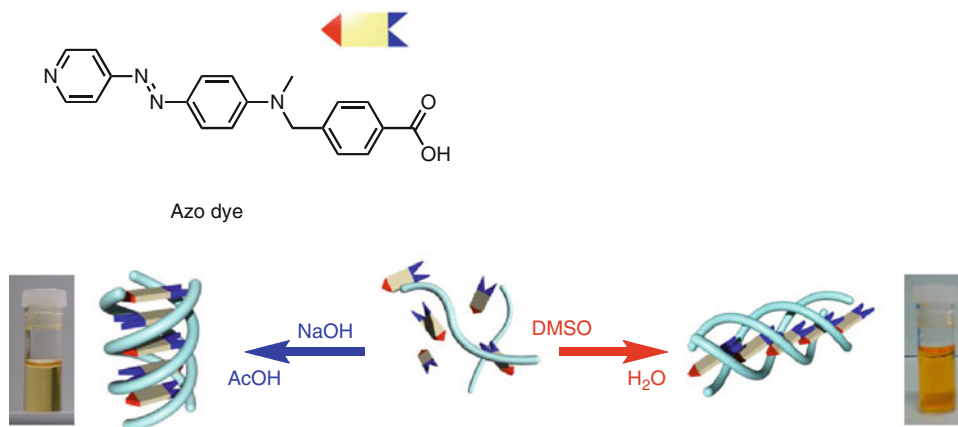
Azo dye

Fig. 17 a UV–VIS and **b** CD spectra of the samples containing Azo dye/SPG composite (*blue lines*), monomeric Azo dye in DMSO (*black line*) and Azo dye aggregate in water/DMSO mixed solvent (*red lines*), preparing from DMSO solution, 1.0 cm cell length, room temperature, **c** photo image of the solution containing Azo dye/ SPG composite and **d** schematic illustration of the J-type assembly formation during the renature of s-SPG: this type of assembly would be created as a major component in the solution. Reprinted with permission from Ref. [106] (Color figure online)
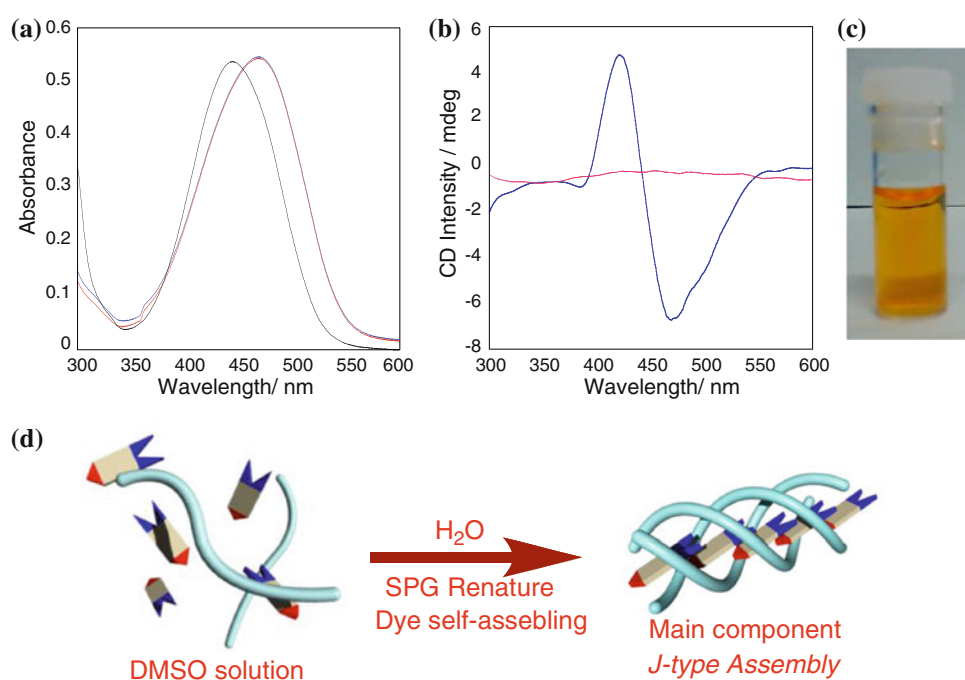
process of alkaline s-SPG solution, where π–π stacking and dipolar–dipolar interactions become the major driving forces instead of hydrogen-bonding interactions. The triple strand of SPG is dissociated into the single strand at pH >12, whereas it retrieves the original triple strand by pH neutralization. To the NaOH solution containing s-SPG and azo-dye, of which carboxylic acid terminal dissociates to its carboxylate anion form, aqueous acetic acid was gradually added to give a clear yellow solution, adjusting the final pH to 7.0. The absorption maximum of the resultant aqueous solution is blue-shifted from 446 nm to 417 nm with accompanying the slight peak broadening. This blue-shift is ascribed to the creation of the H-type assembly. Furthermore, ICD is also detected at the π–π* transition region of azo-dye assembly, indicating that the one-dimensional H-type assembly is entrapped in the helical SPG cavity, where π–π stacking and dipolar–dipolar interactions in

addition to hydrophobic interactions would become major driving forces (Fig. 18). From these results, it can be concluded that the different dye assemblies are created from azo-dye through the different renaturating process of SPG template. This phenomenon can be regarded as a sort of "polymorphism" induced by the presence of SPG. The creation of the similar dye assemblies has been achieved by using porphyrin derivative, where a J-type porphyrin assembly is also entrapped into the helical SPG cavity [107].

Chemical modification of curdlan toward hemi-artificial functional nanomaterial

As mentioned in the forgoing section, we have synthesized a series of chemically modified SPGs bearing various molecular recognition moieties and showed that these

Fig. 18 a UV–VIS and **b** CD spectra of the samples containing Azo dye/SPG composite (*blue lines*), monomeric Azo dye in DMSO (*black line*) and Azo dye aggregate in water/DMSO mixed solvent (*red lines*), preparing from NaOH solution, 1.0 cm cell length, room temperature, **c** photo image of the solution containing Azo dye/SPG composite and **d** schematic illustration of the H-type assembly formation during the renature of s-SPG: this type of assembly would be created as a major component in the solution. Reprinted with permission from Ref. [106] (Color figure online)
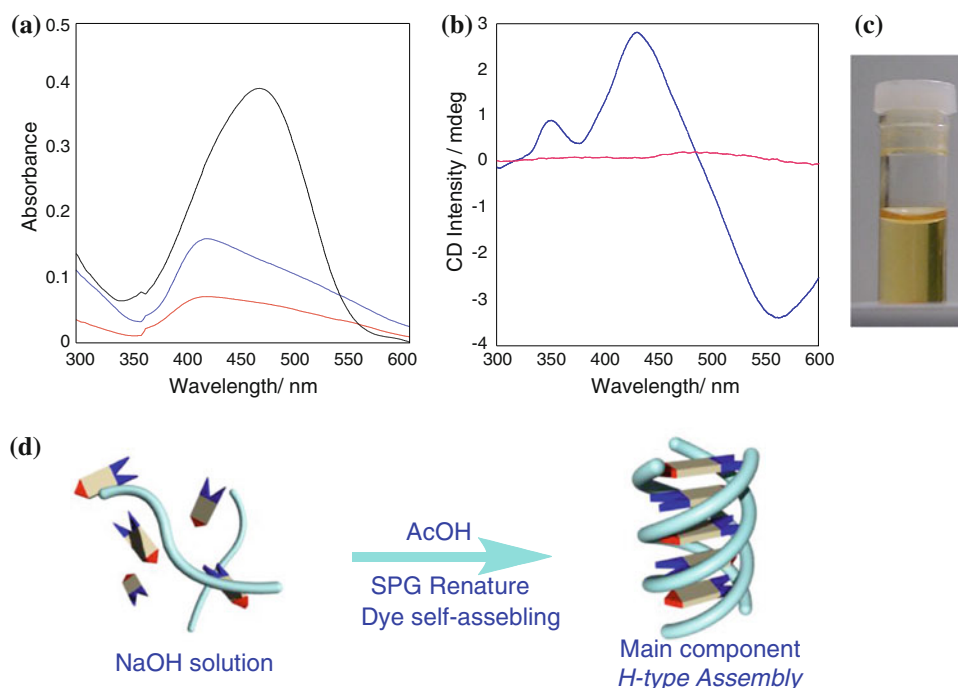
SPGs exert the unique wrapping ability toward hydrophobic functional polymers [36, 39–43]. Aiming at the practical application of the resultant composites as functional nanomaterials, CURs should be more attractive than SPG in the light of low-priced natural materials. CUR has one primary OH group in its repeating unit, appending at C-6, i.e., 6-OH group, which would be an active nucleophile under appropriate reaction conditions, making the selective modification of 6-OH groups possible. Recently, we have successfully demonstrated that the quantitative reaction can be achieved through the azideation reaction of 6-OH, followed by "click reaction", which involves a Cu(I)-catalyzed chemoselective coupling between organic azides and terminal alkynes [44, 45]. This newly exploited strategy allows us to directly introduce various functional groups into 6-OH groups of CUR, leading to the creation of functional materials based on CUR (Scheme 1) [37, 38, 44–46]. The advantageous point of this method is that a series of reaction proceed quantitatively and selectively at 6-OH groups, implying that all 6-OH groups of CUR can be converted to functional groups. Therefore, as described in the forgoing section, there is discrepancy between chemically modified CURs and SPGs in their chemical properties: the modification percentage of the side glucose groups is, at most, 30%.

Taking these facts into considerations, the wrapping of the guest polymer by the chemically modified SPG can be regarded as novel functionalization way through a supramolecular manner. Actually, as described in the previous section, chemically modifed SPGs can bestow the

molecular recognition affinities to SWNT and PANI fibers by just wrapping them [59, 61, 65]. Along the same line, chemically modified CURs should functionalize the incorporated guest polymers by just wrapping them. In particular, the quantitative conversion of 6-OH groups to self-assembling groups allows the resultant composite to self-organize through the surface–surface interactions among the composites. These findings lead to the perspective that the one-dimensional composites prepared from chemically modified CURs act as building blocks for creating the further hierarchical architectures.

Hierarchical assemblies: one-dimensional composite as a building block toward further organization

Among various functional groups introduced into 6-OH groups of CURs, ionic groups are of significantly interest because the electrostatic repulsion among the ionic groups on the CUR surface would provide strong influence on its conformation in water. When single-stranded conformation is transformed to tied triple-stranded in water, the electrostatic repulsion would causes the destabilization of the triple helix. Additionally, natural CURs, which scarcely dissolve into water, can be converted to totally water-soluble polysaccharide such as SPGs. These findings imply that the modified CURs have a potential acting as a one-dimensional host even without the denature/renature processes in water. Accordingly, we have synthesized two kinds of modified CURs with complementary recognition

sites, i.e., trimethyl ammonium or sulfonium groups, making the obtained one-dimensional composites versatile building blocks for further supramolecular assemblies.

Creation of highly-ordered assemblies using functional polymers as building blocks, is of great concern due to their potential applications as fundamental nanomaterials. The difficulty self-assembling system of polymers arises from how one can introduce self-assembling capabilities into a polymer backbone without losing its inherent functionality and from how one can assemble polymers through specific interpolymer interactions without the influence of the nonspecific bundling nature. To overcome the difficulty in polymer self-assembling system, much effort has been paid to exploit a versatile strategy to create hierarchical nanoarchitectures from polymer building blocks. Nevertheless, only a few attempts have been reported for the creation of such hierarchical architectures from polymers [108–110]. The unique hosting ability of β-1,3-glucans, as described forgoing sections, has several lines of advantage to overcome these difficulties in polymer manipulation: that is, (1) when chemically modified β-1,3-glucans are used as one-dimensional hosts, the exterior surface of the resultant nanocomposites can be utilized as an interaction site for the construction of supramolecular architectures and (2) the strong interpolymer interactions among guest polymers are perfectly suppressed by the wrapping effect of β-1,3-glucans, which insulates one piece of guest polymer to maintain its original functionality. As a preliminary example, two kinds of complementary semi-artificial CURs, i.e., CUR–N$^+$ and CUR–SO$_3^-$ were utilizing as a functional sheath for SWNTs, expecting that the mixture of these two composites in an appropriate ratio results in the creation of a hierarchical SWNTs architecture due to the electrostatic interaction (Fig. 19) [111]. It would be important to mention here that CUR–N$^+$ and CUR–

SO$_3^-$ have the similar wrapping capability for SWNTs, suggesting that SWNT/CUR–N$^+$ composite and SWNT/CUR–SO$_3^-$ composite may be used as "complementary" one-dimensional building blocks to create higher-order hierarchical self-assembled architectures (Fig. 19).

SWNT/CUR–N$^+$ and SWNT/CUR–SO$_3^-$ composite solutions containing the same concentration of SWNT were prepared according to the same procedure described in the previous section. The zeta-potential value of an aqueous solution containing SWNT/CUR–N$^+$ composite was estimated to be $+48.9$ mV, whereas an aqueous solution containing SWNT/CUR–SO$_3^-$ composite showed -49.5 mV. Once these two solutions were mixed in the same volume under the very diluted condition, the zeta-potential value of the resultant mixture showed -0.53 mV without accompanying precipitate formation, indicating that the potential charges on these composites are almost neutralized to give a self-assembling composite through the electrostatic interaction. AFM images revealed that the resultant solution contains a well-developed sheet-like structure with micrometer-scale length, which is entirely different from the very fine fibrous structures observed for individual SWNT/CUR–N$^+$ and SWNT/CUR–SO$_3^-$ composites (Fig. 20). These sheet-like structures shows the characteristic Raman peaks at 262 cm^{-1} and 1592 cm^{-1} being ascribed to SWNTs.

TEM is a powerful tool to study how SWNTs are arranged in the obtained sheet-like structure. In the TEM images shown in Fig. 21, it can be recognized that the sheet-like structure is composed of highly-ordered fibrous assemblies. Furthermore, the electron diffraction pattern (inset in Fig. 21b) reveals that the fibrous assembly has some crystalline nature, suggesting that cationic and anionic composites are tightly packed through the electrostatic interaction. The periodicity of the dark layer is

Fig. 19 Proposed concept for creating the hierarchical SWNT architecture form the one-dimensional building blocks through the electrostatic interaction. Reprinted with permission from Ref. [111]
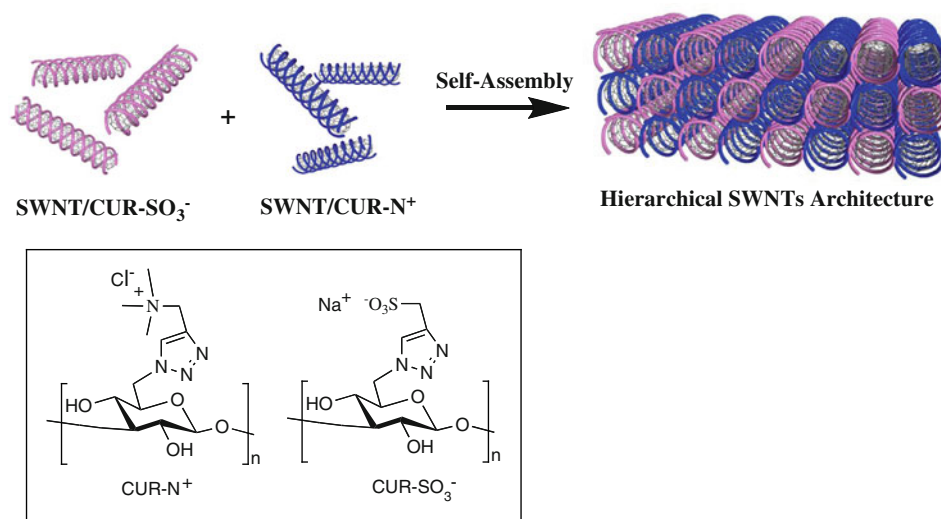
Fig. 20 AFM images of **a** SWNT/CUR–N$^+$ composite and **b** SWNT/CUR–SO$_3^-$ composite, respectively. **c** Magnified AFM image of (**b**). **d** AFM image of the sheet-like structure after mixing SWNT/CUR–N$^+$ composite and SWNT/CUR–SO$_3^-$ composite. **e** Height profile of the sheet-like structure: the AFM tip was scanned along the *black line*. In this AFM image, the thickness of each thin layer is estimated to be ca. 3.5 nm. Reprinted with permission from Ref. [111]
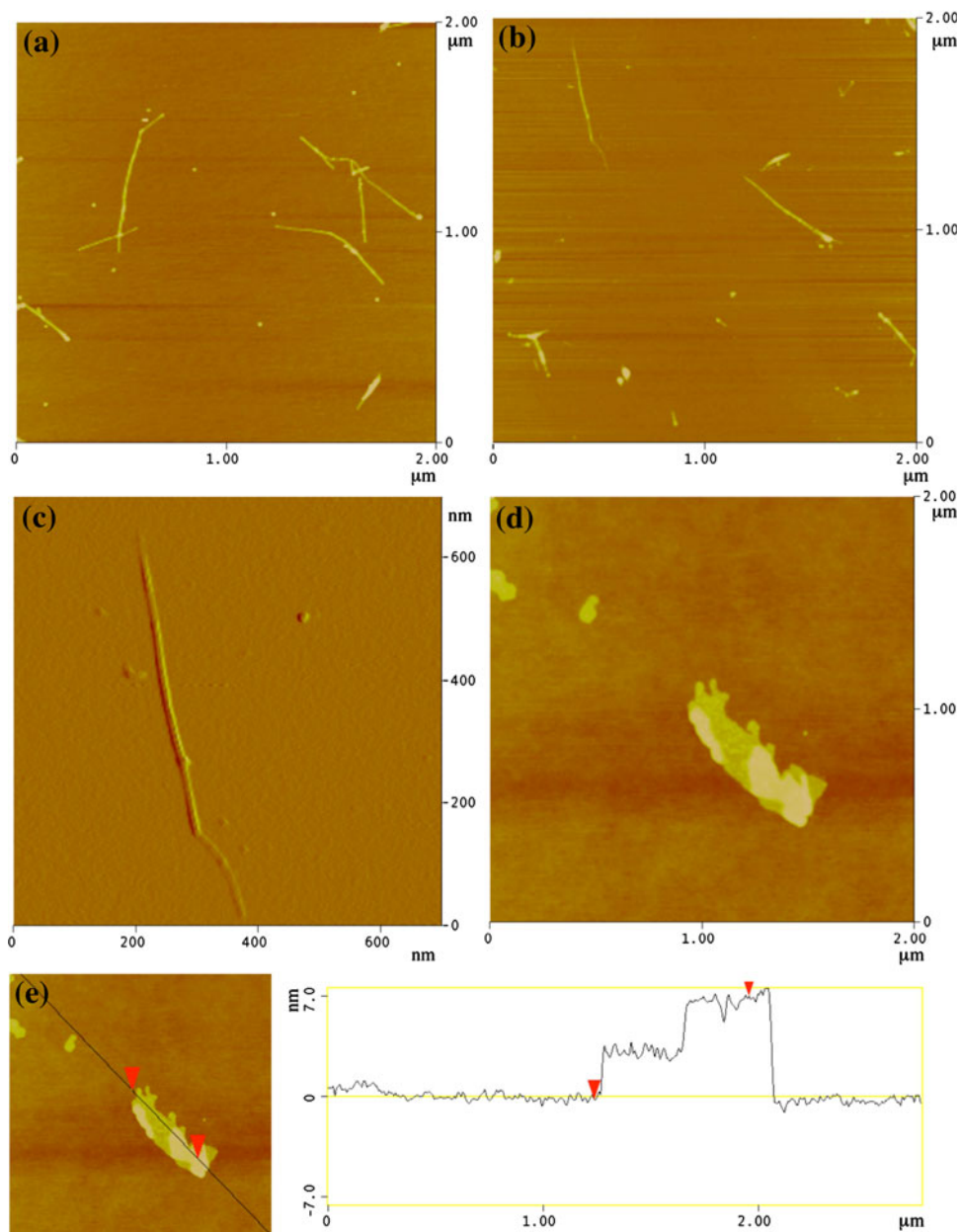
estimated to be ca. 2 nm, which is almost consistent with the diameter of the individual composite obtained by the AFM height profile. These results reasonably lead to the conclusion that the novel strategy toward the creation of "hierarchical" functional polymer architectures can be established by utilizing the complementary semi-artificial β-1,3-glucans as "building blocks".

The mixture of the oppositely-charged small molecules tends to result in nonspecific irregular assemblies through electrostatic interactions, but when either cationic or anionic polymer exists excessively, specific regular structures with the well-controlled size and assembling number can be created. This concept may be applicable

to the present polymer assembling system. When an aqueous SWNT/CUR–N$^+$ composite solution was mixed with an excess amount of an aqueous SWNT/CUR–SO$_3^-$ composite solution, adjusting the (SWNT/CUR–N$^+$)/(SWNT/CUR–SO$_3^-$) ratio to 1/5, bundled SWNTs architectures composed of highly-ordered fibrous assemblies were obtained. The diameter of the bundle structure became larger, with increasing (SWNT/CUR–N$^+$)/(SWNT/CUR–SO$_3^-$) ratio from 1/5 to 1/3. These results indicate that the self-assembling hierarchical architecture is predictable and controllable by tuning the ratio of SWNT/CUR–N$^+$ composite and SWNT/CUR–SO$_3^-$ composite (Fig. 22).
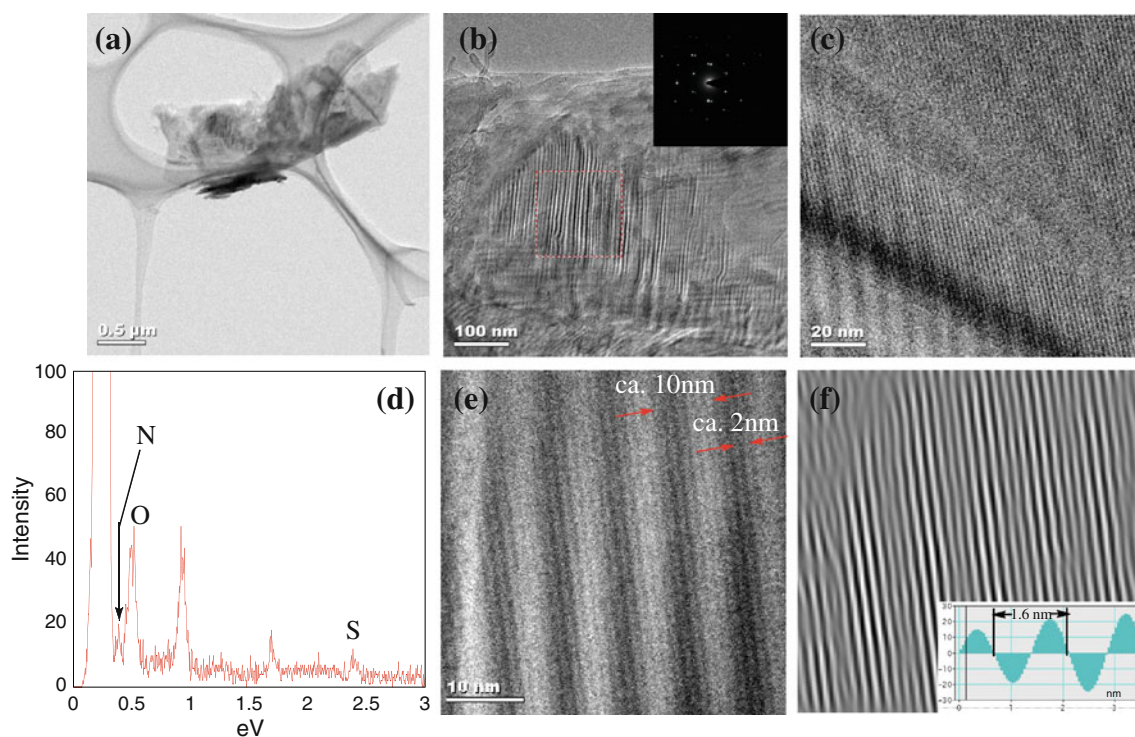
Fig. 21 TEM image of **a** sheet-like structure (*low magnification*), **b** and **c** magnified images of the thin layer (inset: electron diffraction pattern obtained from the sheet). **d** Elemental analysis of the sheet-like structure based on EDS. The spectrum was corrected from the red-square in (**b**). **e** Magnified TEM image of the sheet-like structure containing several thin layers. **f** Fourier translation image of (**d**) and extracted periodical patterns. Reprinted with permission from Ref. [111] (Color figure online)

A new class of polymer-small molecule hierarchical nanoarchitecture: mutual template effect of cationic one-dimentional composite and anionic supramolecular nanofiber

It has been known that tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS^{4-}) generates the di-acid form (H_4TPPS^{2-}) under the acidic conditions, i.e., below pH = 3.0, where pKa value of H_2TPPS^{4-} is 4.9, and therefore tends to self-assemble into the well-regulated fibrous structure (J-aggregate) through electrostatic interactions [112–115]. As the resultant supramolecular nanofiber structure carries anionic charges arising from the sulfonate groups, it would be useful as a supramolecular 1-D building block to form a hierarchical composite with CUR–N^+ or its SWNT composite. It thus occurred to us that the self-assembly of H_4TPPS^{2-} molecules and the cationic CUR–N^+/SWNT composites would result in the hierarchical self-organization of SWNTs, where the H_4TPPS^{2-} J-aggregates act as a supramolecular adhesive agent for the composites (Fig. 23) [116].

We then mixed CUR–N^+/SWNT composites with H_4TPPS^{2-}-containing solution to form H_4TPPS^{2-} J-aggregate on the CUR–N^+/SWNT composite, which would lead to the self-organization of SWNTs due to electrostatic interaction. When the (trimethylammonium)/(sulfonate) ratio was increased from 0.0 to 0.67, the Soret- and Q-bands of monomeric H_4TPPS^{2-} gradually decreased and new peaks assignable to J-aggregate appeared at 490 nm and 710 nm, as shown in Fig. 24. As a reference experiment, we have confirmed that there is no specific interaction between SWNTs and H_4TPPS^{2-} at the same conditions. CD spectral changes strongly support the view that H_4TPPS^{2-} molecules form J-aggregate on the CUR–N^+/SWNT composite, as shown in Fig. 24, being affected by chiral CUR–N^+. The split-type of ICD signals appears at 490 and 498 nm and the cross section wavelength of the peaks is consistent with the absorption maximum of H_4TPPS^{2-} J-aggregate. Beside, the CD intensity also reached to the maximum when the (trimethylammonium)/(sulfonate) ratio was at 0.67, implying that H_4TPPS^{2-} molecules self-assemble on the CUR–N^+/SWNT composite through the electrostatic interaction, leading to the creation of the J-aggregate structure. TEM observation revealed that the H_4TPPS^{2-} J-aggregate formation on the CUR–N^+/SWNT composite [(trimethylammonium)/(sulfonate) = 0.50] leads to the creation of the sheet-like nanostructure with the width about 20 nm, which
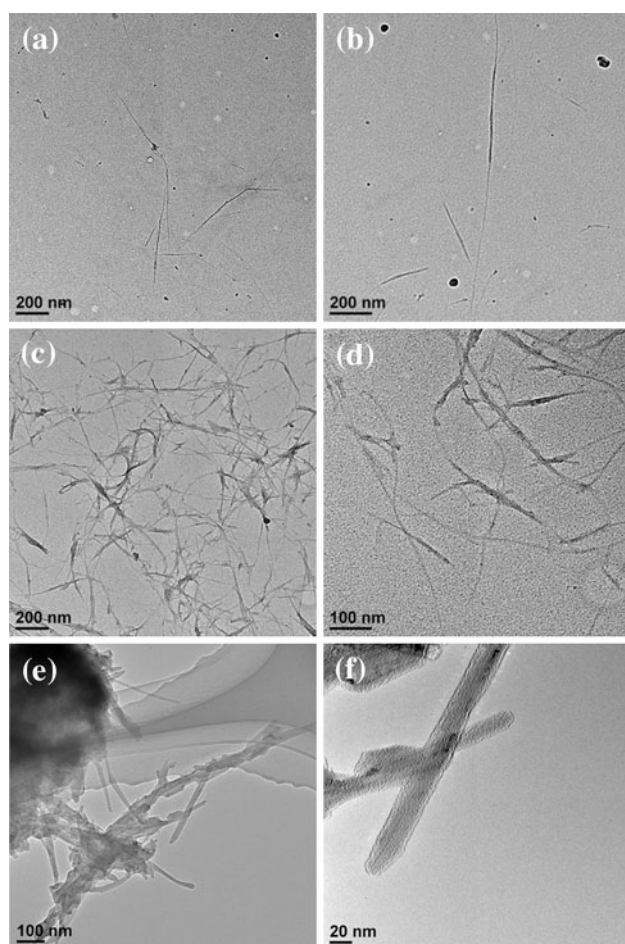
Fig. 22 TEM images of **a** SWNT/CUR–N$^+$ composite and **b** SWNT/CUR–SO$_3^-$ composite. **c** Fibrous bundle structure containing the limited number of SWNTs [(SWNT/CUR–N$^+$)/(SWNT/CUR–SO$_3^-$) = 1/5]. **d** Magnified TEM image of (**c**). **e** Larger bundle structure [(SWNT/CUR–N$^+$)/(SWNT/CUR–SO$_3^-$) = 1/3]. **f** Magnified TEM image of (**e**) (inset: extracted periodical patterns obtained along the *red line*). Reprinted with permission from Ref. [111] (Color figure online)
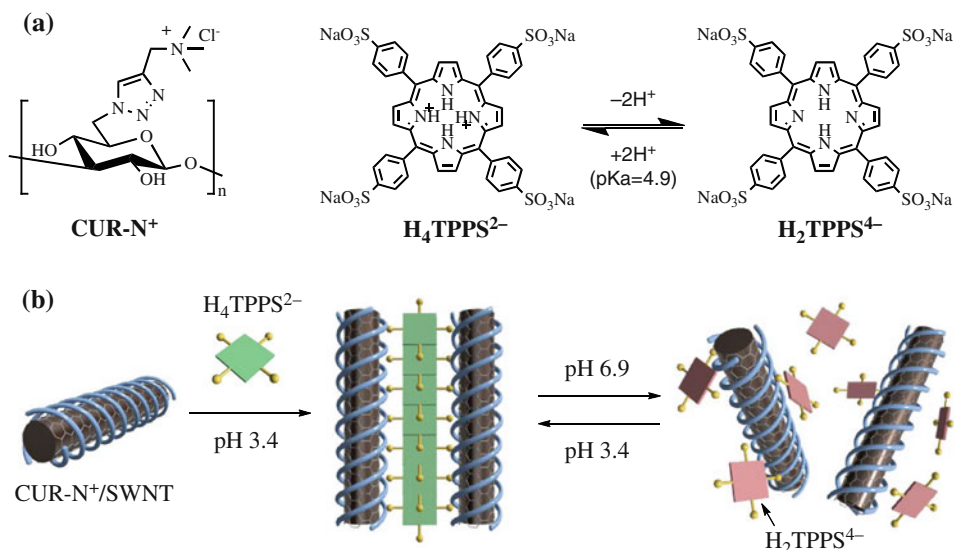
corresponds to the aggregate of several tens CUR–N$^+$/SWNT composites. In addition, the length of the sheet-like structure can be estimated to be *ca.* 1 μm, the value of which is almost consistent with the average length of used SWNTs (0.8–1.2 μm), indicating that the CUR–N$^+$/SWNT composite acts as a 1-D building block.

When the solution containing the sheet-like nanostructures [(trimethylammonium)/(sulfonate) = 0.5] was neutralized by NaOH aqueous solution, the dissociation of H$_4$TPPS^{2-} J-aggregates into monomeric H$_2$TPPS^{4-} occurred. The absorption peaks assignable to H$_4$TPPS^{2-} J-aggregate was also dramatically decreased with increasing pH values, and a new peak assignable to monomeric H$_2$TPPS^{4-} was appeared at 414 nm. The split-type ICD also disappeared during this treatment, suggesting that H$_2$TPPS^{4-} molecules no longer interact with the cationic CUR–N$^+$/SWNT composite. TEM observation supports the view that the sheet-like nanostructures consisting of CUR–N$^+$/SWNT composites are transformed to the individual fibrous assemblies with several nanometer widths (Fig. 25). Interestingly, when the pH value of the solution mixture was restored to 3.4, the sheet-like nanostructure was reconstructed and the original absorption spectral peaks assignable to the J-aggregate emerged again.

We have established a new class of self-assembled nanoarchitecures consisting of cationic one-dimensional composite and anionic supramolecular nanofiber structure. In the present system, the dynamic association/dissociation ability of the porphyrin-based supramolecular nanofibers leads to the creation of various hierarchical polymer assemblies through their structural conversion, which could not be realized only by covalent-bond-based polymer components.

Fig. 23 The schematic illustration of the present system: mutual template effect of cationic polymer composite and anionic supramolecular nanofiber

Fig. 24 UV–Vis (**a**) and CD (**b**) spectral changes of H_4TPPS^{2-} upon addition of only CUR–N$^+$/SWNT composite: 25 °C, 1.0 cm cell
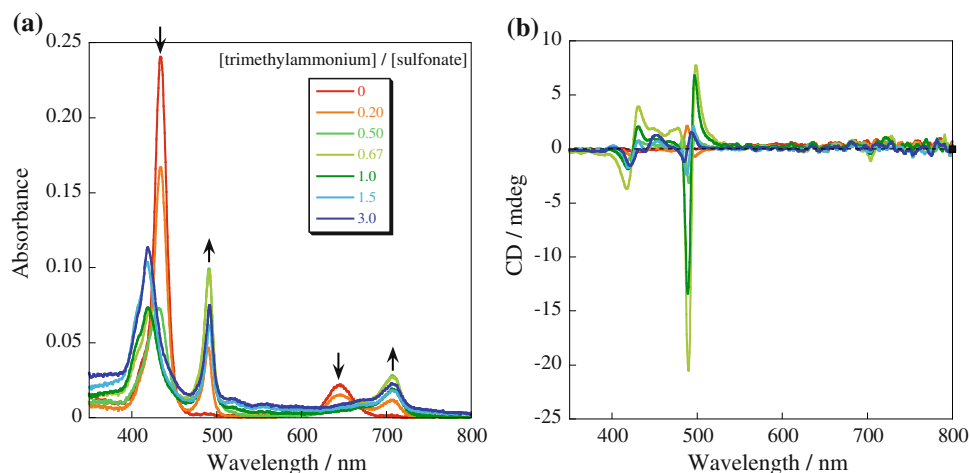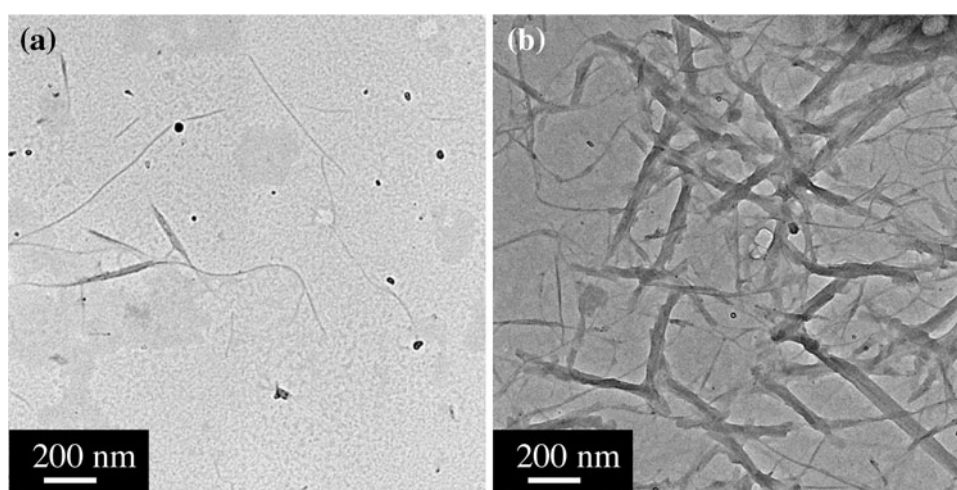

Fig. 25 TEM images of the dissociated structure at pH 6.9 (**a**) and the reconstructed sheet-like structures at pH 3.4 (**b**)

Summary

Most polymer–polymer or polymer–molecule interactions, except those occurring in biological systems, have been considered to take place in a random fashion and to produce morphologically uninteresting polymer-aggregates. In contrast, β-1,3-glucans can interact with polymer or molecular guests in a specific fashion and construct well-regulated one-dimensional superstructures: in the present system, we can expect how β-1,3-glucans wrap these guests. Furthermore, the wrapping occurs in an induced-fit manner, so that various functional nanocomposites can be created, reflecting the inherent functionalities of the entrapped guest materials. These unique features of β-1,3-glucans mostly stem from strong helix-forming nature and reversible interconversion between single-stranded random coil and triple-stranded helix. It should be emphasized that the resultant composite can be applied to biomaterials due to the inherent bio-compatibility of β-1,3-glucans.

The clear wrapping mode allows us to utilize the composite as a one-dimensional building block for further molecular recognition event occurring on the composite surface: the selective modification of β-1,3-glucans endows the composite with molecular recognition and self-organization abilities. We have demonstrated that the wrapping of the chemically modified SPG provide a novel strategy to create functional polymer composites with various molecular recognition tags in a supramolecular manner. Especially, the quantitative conversion of 6-OH groups of CUR to self-assembling groups allows the resultant composite to self-organize through the specific surface–surface interactions among the composites, where the composite acts as one-dimensional building blocks for creating the further hierarchical architecture. Considering the serious difficulties in the creation of hierarchical architectures from synthetic polymers, the present system can open new paths to accelerate development of the polymer assembly systems and can extend the frontier of polysaccharide-based functional nanomaterials.

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