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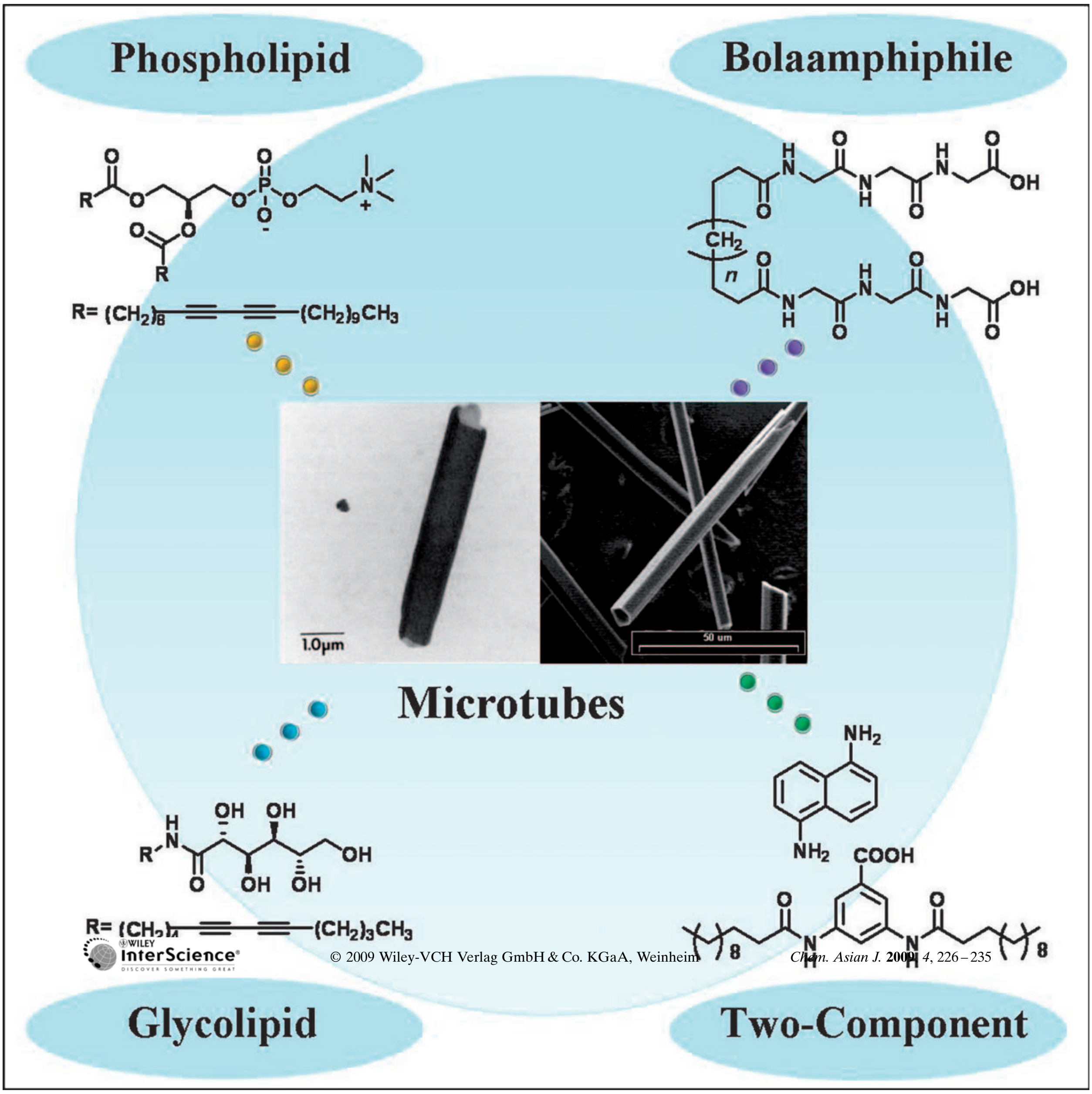
Self-Assembled Organic Microtubes from Amphiphilic Molecules

Ho Yong Lee, Seong Ryong Nam, and Jong-In Hong*[a]



Abstract: In recent years, there have been increasing numbers of reports about self-assembled nano- or microtubular structures, because they have potential uses in nanofabrication, purification, medical, and encapsulation applications. A wide range of tubular structures have been constructed by the self-assembly of amphiphilic molecules in aqueous solution or organic solvents. The diameters of self-assembled tubular structures range between 10 nm and 30 µm. One of the most important factors that determine their suitability for technical applications is the size of the tubes. Therefore, analyzing and sorting tubular structures according to their size is essential. This Focus Review highlights microsized self-assembled organic tubular structures formed in aqueous solutions and organic solvents.

Keywords: amphiphiles · microtubes · nanostructures · phospholipids · self-assembly

1. Introduction

Since the discovery of multi- and single-walled carbon nanotubes,[1] numerous efforts have been directed towards the fabrication of organic and inorganic nanostructures. Self-assembly has been widely used for the fabrication of numerous nano- and microstructures, such as micelles,[2] vesicles,[3] ribbons,[4] fibers,[5] and tubes.[6] Among them, tubular structures have received considerable attention because of their potential uses in guest encapsulation, nano- or microelectronic, magnetic template, and medical applications.[7] After the simultaneous discovery of self-assembled lipid tubules by three research groups in the United States and Japan,[8] many amphiphilic molecules have been designed and used for the fabrication of tubular structures in aqueous solutions. Furthermore, there are increasing numbers of reports on tubular structures produced by self-assembly in organic solvents.

The diameters of self-assembled tubular structures range from 10 nm to 30 µm. Tubular structures have a wide range of sizes compared to typical carbon nanotubes. The size of the tubes (outer and inner diameters, lengths, and wall thickness) and functional groups on the tubular walls are directly related to their suitability for technical applications. Therefore, analyzing and sorting tubular structures according to their size and functional groups is very useful.

Self-assembled tubular structures have been discussed in several review articles.[7a,9] This Focus Review will concentrate on self-assembled organic microtubular structures having a large size above 100 nm (Figure 1), except for the tubular structures based on copolymer amphiphiles. Microtubes constructed from phospholipids, glycolipids, bolaamphiphiles, other one-component systems, and two-component systems in organic solvents will be discussed. We use the term "microtube" to avoid confusion with biological microtubules.

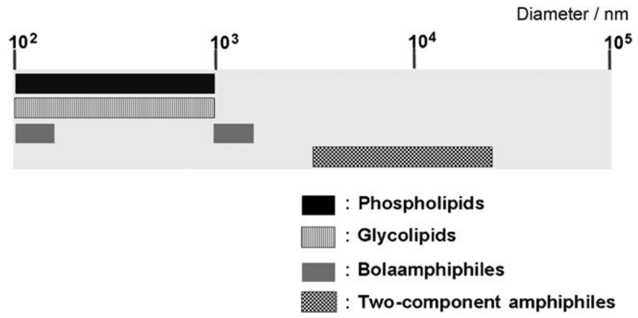


Figure 1. Diameter distribution of microtubes derived from various amphiphiles.

2. Phospholipid Microtubes

Microtubes constructed by self-assembly of the polymerizable diacetylenic phospholipid **1** (Figure 2) have been widely studied.[8a,10] Microtubes have been obtained by the cooling of a saturated ethanolic/water solution of **1**. The tubular structures had diameters of around 0.5 µm and lengths between 50 and 200 µm. The length of the tubes can be controlled by the solvent composition[11] and by adjusting the cooling rate.[12] Singh showed that nonacetylenic lipids did

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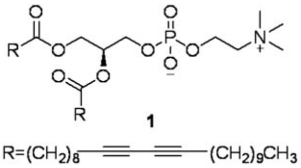
[a] H. Y. Lee, S. R. Nam, Prof. Dr. J.-I. Hong
Department of Chemistry, College of Natural Sciences
Seoul National University
Seoul 151-747 (Korea)
Fax: (+82) 2-889-1568
E-mail: jihong@snu.ac.kr

not form a tube and that the position of a diacetylenic group had little effect on the tubular structure.[7a]

The chirality of the glycerol-derived backbone is directly related to handedness of the tube. The *R* enantiomer produces tubes with a righted-handed exterior helical trace and vice versa. There have been several approaches that can explain the relation between the chirality of the molecules and the self-assembled tubular structures. A theoretical consideration of the tube formation has been introduced and discussed in detail in reviews by Schnur and Shimizu.[7a,9] Therefore, we will not detail it in this Focus Review. Clark et al. performed an optical microscopic study of **1** under slow cooling conditions.[13] They proved that right- and left-handed structures were formed in equal amounts in the initial step of tube formation (Figure 2). They suggested that the effect driving the helix formation was not directly related to the molecules chirality.



1

$R=(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_9CH_3$

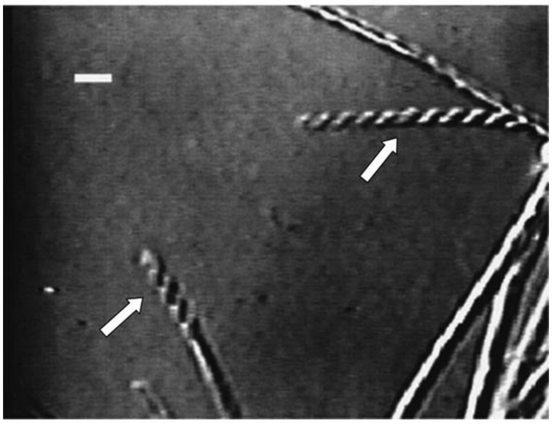


Figure 2. Nomarski DIC microscopy video frame obtained while cooling at 0.25 °C, showing the simultaneous growth of left- (right arrow) and right-handed (left arrow) helical ribbons. Scale bar: 1 μm. Reproduced with permission from reference [13].

Thomas et al. have examined the effects of modifying the glycerol backbone of **1** on the tube diameter and helicity.[14]

Phosphonate **2** (Figure 3), which replaces the phosphoryl oxygen atom linking the glycerol backbone to the phosphocholine head group with a methylene group, yielded microtubes each having an external diameter increased twofold (1.18 μm) and a tube wall thickness that was half of those of the microtubes originating from **1**. Interestingly, phosphonate **2** simultaneously self-assembled into right- and left-handed tubular structures, despite an enantiomerically pure form having been used (Figure 3). Phosphonate **3**, which has one methylene group less than **2**, produced similar microtubes with left- and right-handedness. The external diameters (1.07 μm) were increased approximately twofold compared to microtube **1**. However, the tube length and membrane thickness decreased. These results suggest that just small changes in the starting molecules have pronounced effects on the helicity, diameters, length, and thickness of self-assembled tubular structures.

Negatively charged phospholipids **4, 5, 6**, which are modified with several glycols in the head group, produced mirco-

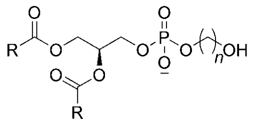
Abstract in Korean:

최근 들어 다양한 종류의 유기튜브 구조가 수용액이나 유기용매에서 친양쪽성체 분자의 자기조립에 의하여 만들어질 수 있음이 알려져 왔다. 이렇게 만들어진 나노 혹은 마이크로 크기의 튜브 구조는 기술적으로나 혹은 의학적으로 다양하게 응용될 수 있다. 튜브의 크기는 튜브의 기술적 응용성을 결정하는데 중요한 요소임으로, 유기 튜브 구조를 크기에 따라 분석하고 정리하는 것은 중요한 작업이라고 볼 수 있다. 따라서, 본 리뷰에서는 마이크로 크기의 자기 조립된 유기 튜브 구조를 체계적으로 정리하였다.

Jong-In Hong *was born in 1959 in Daegu, Korea and received his PhD from Columbia University in 1990 with Professor W. Clark Still. After postdoctoral studies with Professor Julius Rebek, Jr. at Massachusetts Institute of Technology (1991–1992), he joined Seoul National University in 1993 as an Assistant Professor, and became Professor in 2004. His research interests entail molecular recognition of biologically significant compounds and the development of self-assembled superstructures based on metal–ligand and noncovalent interactions.*

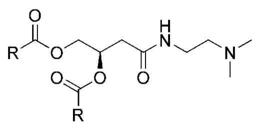
Ho Yong Lee *was born in 1977 in Hwasung, Korea and received his BS from Seoul National University in 2000. He received his PhD from Seoul National University under the direction of Professor Jong-In Hong in 2007. He is currently undertaking postdoctoral studies at Seoul National University. His research interests include the development of self-assembled superstructures based on metal–ligand interactions and the gelation of organic compounds.*

Seong Ryong Nam *was born in 1976 in Anyang, Korea. After he received his BS from Han Yang University in 2002, he joined Professor Jong-In Hong's group at Seoul National University. He is currently a PhD candidate. His research interests include the development of self-assembled superstructures based on noncovalent interactions, and structural studies of organogels.*



4, **5**, **6** (*n*=2, 3, 4)

$R=(CH_2)_8{-}{\equiv}{-}{\equiv}{-}(CH_2)_8CH_3$



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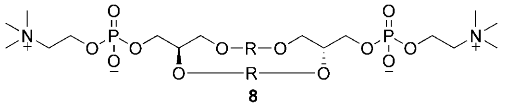
$R=(CH_2)_8{-}{\equiv}{-}{\equiv}{-}(CH_2)_{11}CH_3$



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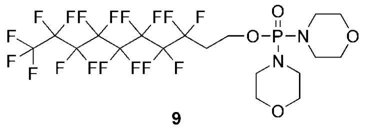
$R=(CH_2)_8{-}{\equiv}{-}{\equiv}{-}(CH_2)_8$



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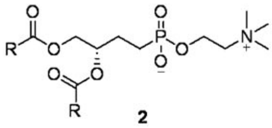

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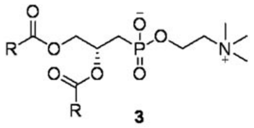


3

$R=(CH_2)_8{-}{\equiv}{-}{\equiv}{-}(CH_2)_9CH_3$

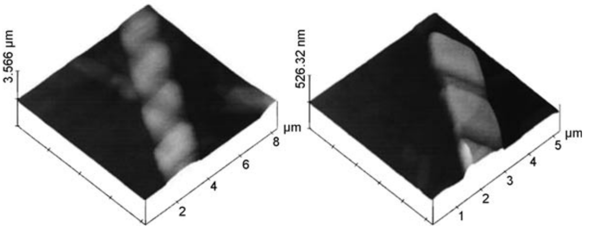
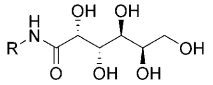


Figure 3. Pseudo-three-dimensional perspective of right-handed (left) and left-handed helices (right) in the same phosphonate preparation, obtained with underwater contact mode AFM. Reproduced with permission from reference [14a].

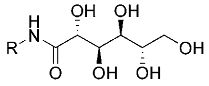
tubes with a wide range of diameters, depending on the head group size, pH, ionic strength, and the metal counteranion.[15] The phospholipid analogue **7**, containing a chiral 1-(*N*,*N*-1-dimethylamino)ethyl-2,3-dihydroxybutyramide head group, self-assembled into microtubular aggregates in acidic solution after 2–3 days.[16] At this time, the length of the tubes ranged from 100 to 400 µm. After about 1 week, tubes with lengths of around 1200 µm were observed. A typical external diameter of the tubes was about 2 µm. Microtubes based on a cyclic phospholipid **8** were reported by Shibakami et al.[17] Their diameters were about 300 nm. Riess and co-workers have reported stable cylindrical aggregates from fluorinated single-chain amphiphiles in which a dimorpholinophosphoramidate, perfluoro-alkylated single-chain surfactant (**9**) was used.[18] This fluorinated surfactant has no rigid segment to promote molecular alignment and no possibility of specific intermolecular interactions. The strong hydrophobic forces resulting from the fluorinated chains alone might be efficient for the formation of microstructures. A dispersion of 6% w/v of the amphiphiles hydrated at 50 °C with gentle swirling by hand yielded rigid tubule-like aggregates within several hours. These microtubes were 0.1 to 0.5 µm in diameter and were typically 10–50 micrometers long.

3. Glycolipid Microtubes

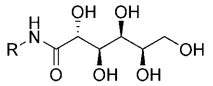
Amphiphiles incorporating sugars in the position of the polar head group, referred to as glycolipids, produce self-assembled tubular structures having diameters from tens of nanometers to hundreds of nanometers. A series of saturated and unsaturated aldonamides (**10**–**15**) were widely studied by O'Brien et al.[19] and Furhop et al.[20] Aldonamides yield various types of morphologies, such as tubes, fibers, helices, and sheets (Figure 4). Table 1 summarizes the diameters and morphologies of the tubes. Unlike phospholipids, both saturated and unsaturated aldonamides self-assembled



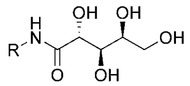
10 and **10a**



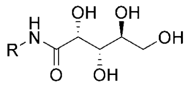
11 and **11a**



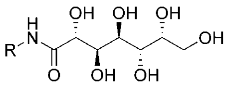
12 and **12a**



13 and **13a**



14 and **14a**



15 and **15a**

10-15 : $R = (CH_2)_4{-}{\equiv}{-}{\equiv}{-}(CH_2)_3CH_4$

10a-15a : $R = (CH_2)_{11}CH_3$

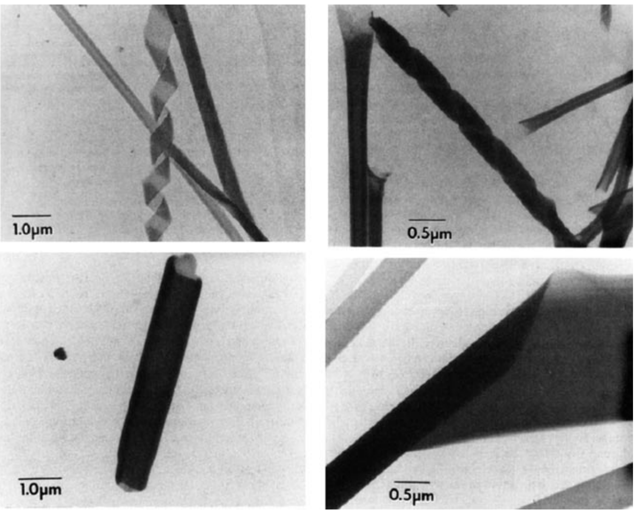


Figure 4. TEM images of gluconamide assemblies of **10** (top left), **15** (top right), **11** (bottom left), **13** (bottom right). Reproduced with permission from reference [19b].

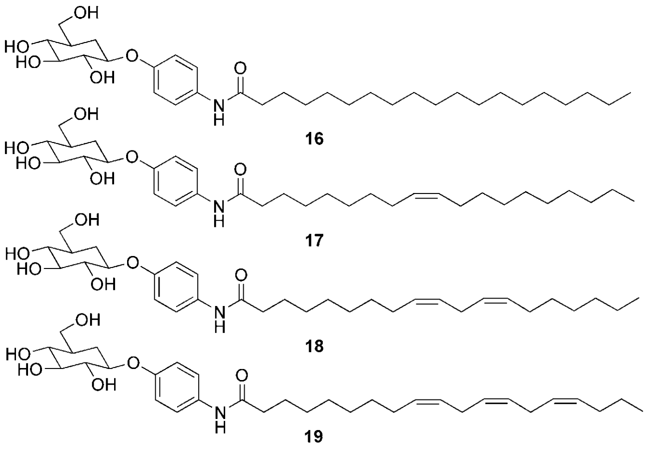
Table 1. The diameters and morphologies of self-assembled microtubes from aldonamides.

Cmpd	Diacetylenic		Dodecyl	
	Diameter [μm]	Morphology	Diameter [μm]	Morphology
10	0.3	helices, tubes	1.0	helices, tubes
11	0.37 ± 0.1	tubes	0.1	helices, tubes
12	0.37 ± 0.15	tubes	n.t.[a]	n.t.
13	0.27 ± 0.09	open and closed tubes	0.4	open and closed tubes
14	n.t.	n.t.	0.4–0.7	helices, tubes
15	0.30 ± 0.1	helices, tubes	n.t.	n.t.

[a] No tubular structures were formed.

into tubular structures. There is no morphological difference between the polymerized and the unpolymerized assemblies from diacetylenic galactonamide and mannonamide. The diameters of the microtubes from diacetylenic aldonamides ranged from 0.3 to 0.4 μm, while the microtubes from dodecyl galactonamide showed an approximate threefold increase in their diameters. According to a previous modelling study,[19b] the head-to-tail packing arrangement and "dromic" hydrogen-bonding patterns are responsible for the fiber-like assemblies, and the head-to-head packing arrangement is associated with planar, helical, or tubular assemblies.

Shimizu et al. have studied the effects of the *cis* double bond on the morphology of self-assembled structures from long-chain phenyl glucosides and *N*-gluconamide derivatives.[21] In their study, a series of phenyl glucosides (**16–19**) self-assembled into nano- or twisted fibers (**16, 17**), helical ribbons (**18, 19**), and tubes (**18, 19**). In the case of **18**, helical ribbon structures, having outer diameters of 80–100 nm, were formed as the major morphology. Tubular structures as the major morphology, having outer diameters of 110–130 nm and wall thickness of 20–30 nm, were obtained in an aqueous dispersion of **19** that possessed three *cis* double bonds.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17
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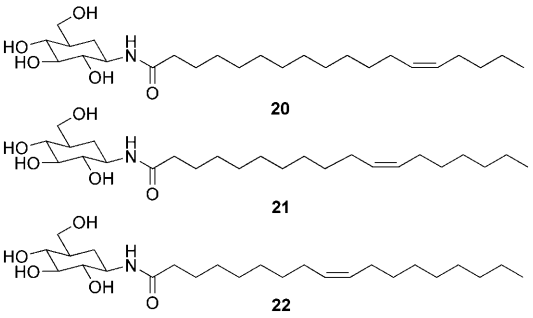
19

Further increasing the position number of a *cis* double bond causes self-assembly into tubular structures only. Also, a correlation between the size distribution of the tube and the position of the *cis* double bond was revealed. This was done by adjusting the position of the *cis* double bond in the C_{18} hydrocarbon chains of glucopyranosylamide lipids (**20–22**). The position of the *cis* double bond had no significant influence on the average outer diameters, but it significantly affected the distribution width (Figure 5). The 11-*cis* derivative (**20**) produced tubes with a narrow diameter distribution among the three compounds **20–22**. This makes it the best candidate if uniformity is required.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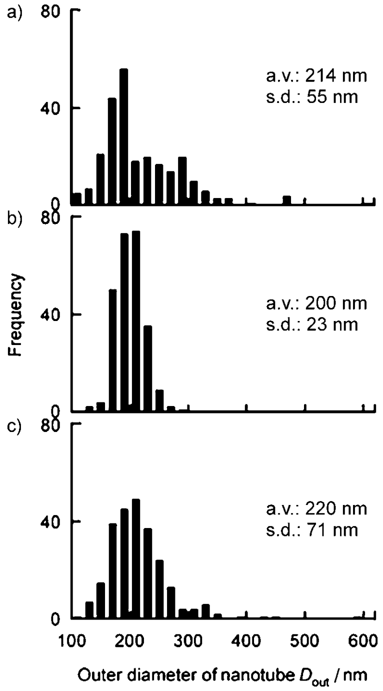
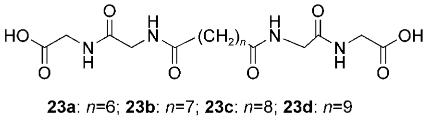


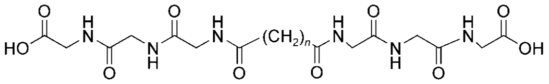
Figure 5. Comparison of histograms for the outer diameters of the self-assembled lipid tubes from the glycolipid **20** (a), **21** (b), and **22** (c). Each histogram was depicted for 250 pieces of tubes. a.v. = average; s.d. = size distribution. Reproduced with permission from reference [21b].

4. Bolaamphiphiles

The self-assembly of bolaamphiphiles into potentially useful nano- and microstructures has been the subject of intense study in recent years.[22] Shimizu and co-workers have reported the self-assembly of vesicles encapsulated by microtubule structures made up of a class of dicarboxylic oligopeptide bolaamphiphiles.[23] Bolaamphiphiles consist of a hydrophobic central oligomethylene chain of various lengths and hydrophilic dicarboxamides with two or three oligoglycine head groups at each end (**23a–h, 24a**,**b**).



23a: n=6; **23b**: n=7; **23c**: n=8; **23d**: n=9
23e: n=10; **23f**: n=11; **23g**: n=12; **23h**: n=14



24a: n=6; **24b**: n=10

When an aqueous solution (sodium salt, 10 mM, pH 7–8) was aged at room temperature for 2–3 weeks, fibrous assemblies could evidently be seen. The phase-contrast light micrograph and laser scanning microscopy revealed well-defined microtube structures with closed ends and uniform diameters (about 1–2 μm, Figure 6). Isolation and dehydration of these tubes did not affect their external appearance, but the closed ends were opened and vesicles leaked out. The tube formation occurred only when the oligomethylene chain had an even number of carbon atoms (**23a, 23c**, **23e**, and **24b**). No microtubes were produced from the oligomethylene chains having odd numbers of carbon atoms, irrespective of the chain length or the presence of longer alkylene chains ($n > 11$).

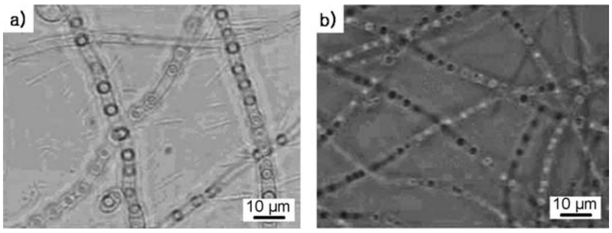


Figure 6. a) Phase-contrast light micrograph and b) dark-field optical micrograph for the vesicle-encapsulated microtubes formed from **23e**. Reproduced with permission from reference [9b].

These peptide bolaamphiphile molecular assemblies are largely influenced by the ionization state of the two terminal carboxy groups. As the diglycyl character can form versatile hydrogen bonds, the bolaamphiphiles gave several kinds of equilibrium mixtures in water, including tubes, vesicles, and crystals. An FTIR study showed that the microtube membrane contains intralayer acid–anion dimers. Vectorial formation of such dimers could be a driving force for the tube formation. Further protonation of the head groups rearranges the hydrogen-bond scheme to form interlayer acid–acid dimers that result in the formation of rodlike micelles, microtubes, and microcrystals.

A possible mechanism for the tube formation is shown in Figure 7. First, anionic bolaamphiphiles form rodlike micelles. According to the protonation process,[23d] efficient aggregation between charged and uncharged species occurs. Thus, the intralayer acid–anion dimers effectively produce a stable lamellar membrane, and curvature may be caused by an asymmetric protonation environment at the outer and inner surfaces of the tube.

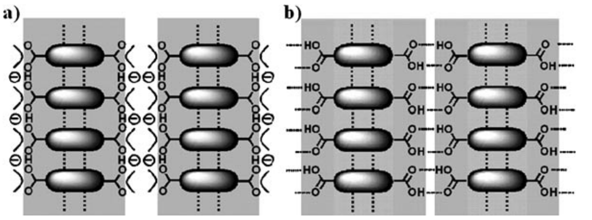
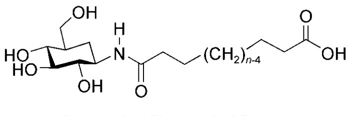


Figure 7. Schematic representation of a) intralayer acid–anion dimers, and b) interlayer acid–acid dimers that result in the formation of rodlike micelles, microtubes, and needle-shaped microcrystals, respectively.

The use of unsymmetrical bolaamphiphiles is the most direct way to construct an unsymmetrical lipid membrane. The nano- or microtubes with different inner and outer lipid membrane surfaces are fascinating architectures applicable to the specific modification of internal and external surfaces. Shimizu and co-workers have reported self-assembled nano- and microtublar structures made up of a class of ω-[*N*-β-D-glucopyranosylcarbamoyl]alkanoic acids with even-numbered oligomethylene chains.[24] The inner diameters of micro- and nanotubes from unsymmetrical bolaamphiphiles (**25a–f**), having a 1-glucosamide moiety at one end of an oligomethylene chain and a carboxylic acid group at the other end, could be controlled by varying the oligomethylene spacer length.



25a: n=12; **25b**: n=13; **25c**: n=14
25d: n=16; **25e**: n=18; **25f**: n=20

Unsymmetrical bolaamphiphiles are able to form a monolayer lipid membrane (MLM). MLMs are categorized into unsymmetrical or symmetrical polymorphs, depending on the packing mode of the components. Four types of multilayer structures, according to the stacking motif of the MLMs, are shown in the top of Figure 8. The stacking periodicity values indicate that the MLMs of microtubes belong to three categories: thin, medium, and thick. The thin membrane consists of an unsymmetrical MLM with head-to-tail (H-T) orientation. The thick membrane consists of an unsymmetrical MLM with H-H orientation. The medium membrane appears to be a symmetrical MLM at each interface. The ratio of the molecular length to the MLM thickness and the oligomethylene chain lengths of compound **25** enabled determination of the polymorph or polytype of the microtubes. The use of transmission electron microscopy (TEM) revealed that compounds **25c–f** formed microtubes (Figure 9). The microtubes were 118–190 nm in outer diameter, 60–90 nm in inner diameter, and up to several hundred micrometers long. The wall thicknesses of the microtubes were 20–40 nm.

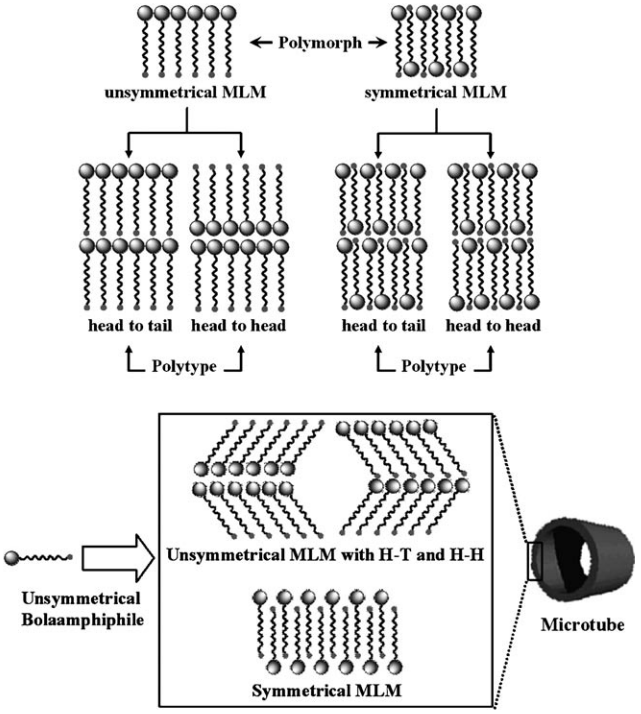


Figure 8. Top) Schematic illustration of monolayer lipid membranes (MLMs) formed from unsymmetrical bolaamphiphiles and the resulting four types of multilayer structures according to the stacking motif of the MLM. The smaller of the two hydrophilic groups is considered to be the tail. Bottom) Lipid tube consisting of monolayer lipid membranes of unsymmetrical bolaamphiphiles.

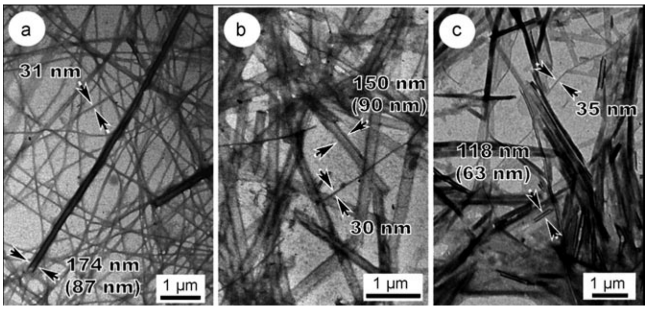
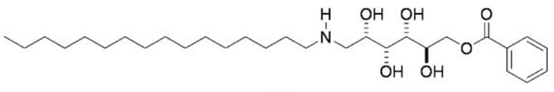


Figure 9. TEM pictures of unstained self-assembled structures showing a mixture of micro- and nanotubes formed from a) **25c**, b) **25d**, and c) **25e**. The numerical values indicate the outer and (in parentheses) inner diameters of the nano- and microtubes indicated by arrows. Reproduced with permission from reference [24].

5. Tubes in Single-Molecule Gels



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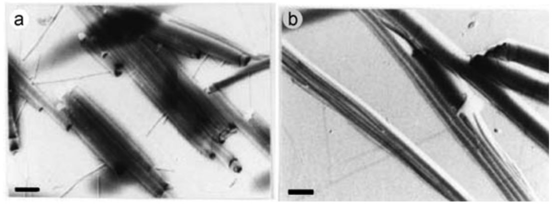
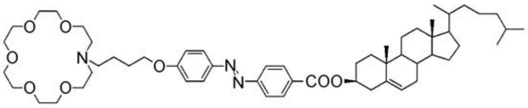


Figure 10. a) TEM image of a gel of **26** in chloroform (Pt shadowing): cigar-like tubes from rolled-up multilayers; scale bar: 1.12 μm. b) TEM images of gel of **26** in chloroform: whisker-type fibers and cigar-like tubes; scale bar: 450 nm. Reproduced with permission from reference [25].



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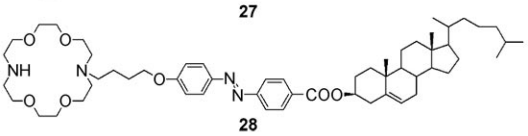

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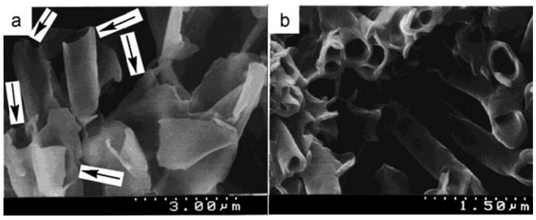


Figure 11. SEM images of xerogels prepared from the cyclohexane gels of **27** (a) and **28** (b). The arrows in (a) indicate pseudocylindrical structures. Reproduced with permission from reference [26].

In the case of single-molecule gelation, there are two previously reported examples of microtubes formed by gelation in organic solvents (Figures 10 and 11). Organogelators forming microtubular structures are known to show poor gelation ability or result in an opaque gel, because microtubular structures might be insufficient to immobilize solvents.

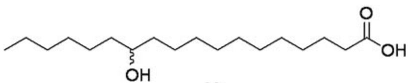
Nolte and co-workers have synthesized various carbohydrate amphiphiles and tested their gelation abilities in organic solvents.[25] For instance, the microscopic structures of *N-n*-alkylgluconamide benzoate esters **26** in chloroform gel were found to be composed of whisker-type fibers and cigar-like tubes. TEM observations revealed that the cigar-like structures resulted from rolled-up multilayers (Figure 10). The cigar-like tubes had external diameters between 0.2 and 0.5 μm.

Shinkai and co-workers have reported microtubes in organogels.[26] The cholesterol-based gelators **27** and **28** did not make strong organogels with cyclohexane when the gelator concentration was between 5.0 and 10.0 wt %. The xerogel of compound **27** exhibited curved lamellar structures and pseudocylindrical structures with 30–40 nm thicknesses (Figure 11). The xerogel of **28** in cyclohexane reveals multilayer tubular structures with walls 45–75 nm long and inner diameters of 170–390 nm. These curved lamellar structures probably have developed into the tubular structures.

6. Two-Component Systems

In the previous sections, we dealt with mircrotubular assemblies with single components, such as lipids, gels, and bolaamphiphiles. Recently, the facile preparation of self-assembled microtubes using a mixture of two components has been reported. The most important features of a two-component system are easy preparation and the facile tuning of structures by changing the molar ratio of the two components, or by changing one of the two components.

Oda et al. reported various nanostructures, such as helical ribbons, flat ribbons, and tubes. They used a combination of gemini surfactants and tartrate counteranions.[4,27] To our knowledge, Nallet's research group first prepared microtubes using a two-component system.[28] An equimolar mixture of *rac*-12-hydroxy-stearic acid (*rac*-**29**) and ethanolamine in water was heated to 75 °C, and then cooled down to room temperature. Phase-contrast micrographs of the resulting turbid liquid solution showed rodlike structures. TEM images of these rods revealed hollow tubular structures with inner and outer diameters of 400 and 600 nm, respectively (Figure 12).



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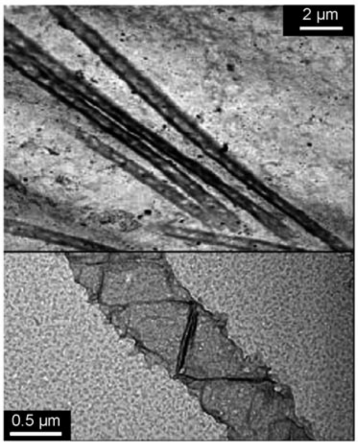
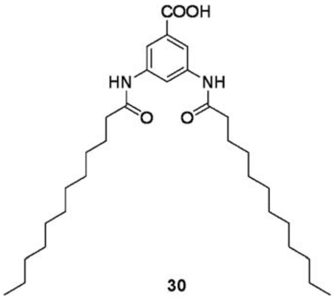


Figure 12. TEM images of a 1 % aqueous dispersion of 12-hydroxystearic acid–ethanolamine salt at room temperature after staining with phosphotungstic acid (top) and uranyl acetate (bottom). Reproduced with permission from reference [28].



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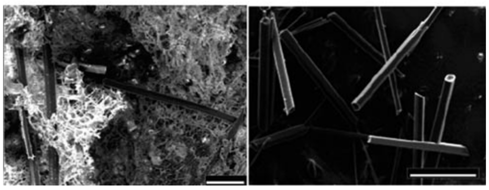
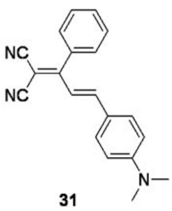


Figure 13. SEM images of dried gel of a mixture of NA and **30** in cyclohexane (left; scale bar: 100 μm) and decalin (right; scale bar: 50 μm). Reproduced with permission from reference [29].

Our research group reported microtubular structures in organic solvents using a two-component system.[29] Homogeneous mixtures of aromatic amines (1,4-phenylenediamine (PA), 1,5-naphthalene-diamine (NA)) and amphiphile **30** in a ratio of 1:2 formed gels in non-aromatic hydrocarbon solvents, such as cyclohexane and decalin. The thermal and morphological properties dramatically changed depending on the sizes and shapes of the aromatic amines. The microstructures of gels formed from mixtures of PA and amphiphile **30** showed typical fiber-like structures (Figure 13). However, in the case of the mixture of NA and amphiphile **30** in cyclohexane and decalin, microtubular structures were observed. The microtubes in cyclohexane had uniform external diameters of 30–40 μm. The length of the longest microtubes was 5 mm. The microtubes in decalin had external diameters of 5–10 μm and lengths of 20–70 μm. The microtubes formed in decalin were faceted, while those formed in cyclohexane were more circular. The change of shape and size of the microtubes implies that the solvent affects the microscopic structure of the gelators. We also obtained various types of microstructures by changing the aromatic and amphiphile groups.

7. Miscellaneous Types

Microtubes constructed by self-assembled organic compounds, without the participation of amphiphiles, were also reported. Lee and co-workers reported a facile route to the fabrication of single-crystalline [2-(*p*-dimethylaminophenyl)ethenyl]phenylmethylene propanedinitrile (DAPMP, **31**) microtubes with a distinctive rectangular cross section.[30] A solution of DAPMP in THF was injected into high-purity water with vigorous stirring. After stirring for 3 min, the sample was stabilized for about 4 h to yield the microstructures. The proposed mechanism of the formation of the microtubes involves the etching or dissolution of the DAPMP solid rectangular nanorods at their centers by THF. This process gradually converts the solid nanorods to microsemitubes and finally to completely hollow tubular structures (Figure 14).



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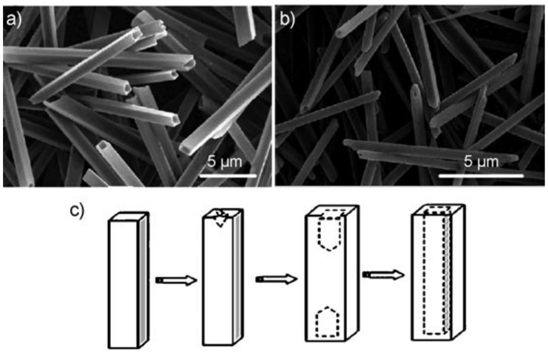
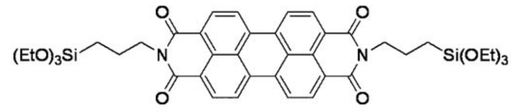


Figure 14. SEM images of microtubes with sizes of a) 1 μm and b) 450 nm. c) Proposed process of tube formation. Reproduced with permission from reference [30].

Carbon and silica are both significant in materials science owing to their importance in both practical applications and academic research.[31] Lu and co-workers reported that perylenediimide-bridged silsesquioxane (PDBS) building molecules demonstrated an interesting assembly behavior in THF/petroleum ether solutions.[32] The solution drying rate and PDBS concentration determined the morphologies and sizes of the assemblies. Tubes with uniform inner and outer diameters in the ranges of 3.7–7 μm and 5–10 μm, respectively, and lengths up to 1 mm, were prepared by casting the PDBS THF/petroleum ether solution on glass substrates at room temperature, with subsequent air drying for about 5 min (Figure 15). The superstructures such as tubes, fibers, and spheres were maintained after carbonization at 950 °C, and were found to show magnificent electrical properties.



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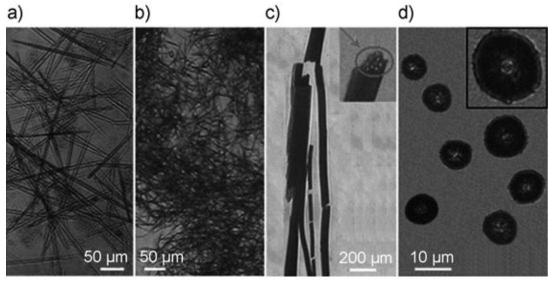

Figure 15. a) Optical micrographs of tubes prepared by casting PDBS THF/petroleum ether solution (PDBS concentration: 8.3 mg mL^{-1}) on a glass substrate at room temperature; b) same conditions as with (a) on a hot glass substrate at about 65 °C; c) a tubular structure produced by very slow evaporation (for about two weeks); d) Hollow spheres after evaporation of PDBS THF/petroleum ether solution (PDBS concentration: 2.7–3.3 mg mL^{-1}) at room temperature. Reproduced with permission from reference [32].

8. Conclusions and Outlook

We have discussed the recent developments in the field of self-assembled organic microtubes. Owing to the developments in the area of self-assembly, we can now obtain all scales of tubular structures from a few nanometers to tens of micrometers. Structural diversities are essential factors determining the extent of applications. Therefore, there is a continuous demand for the development of new building blocks to construct tubular structures. Furthermore, the functionalization of the self-assembled tubes can extend their potential applications. Diverse functional groups can be introduced in the inner and outer walls of self-assembled tubes by modification of the polar head groups of the amphiphiles. Also, highly packed structures on the inside walls of the tubes might result in the development of semiconducting tubes. This may be achieved by the introduction of semiconducting molecules on the hydrophobic chains.

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