

Boroxine Nanotubes: Moisture-Sensitive Morphological Transformation and Guest Release

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Boroxines, (R-BO)₃, which can be easily synthesized via a dehydration reaction of boronic acids, R-B(OH)₂, selectively self-assemble in toluene into nanofibers, nanorods, nanotapes, and nanotubes, depending on the aromatic substituent (R). Spectroscopic measurements show that the nanotube consists of a J-aggregate of the boroxine. Humidification converts the morphology from the nanotube to a sheet as a result of the hydrolysis of the boroxine components and subsequent molecular-packing rearrangement from the J-aggregate to an H-aggregate. Such a transformation leads to the compulsive release of guest molecules encapsulated in the hollow cylinder of the nanotube. The hydrolysis and the molecular-packing rearrangement described above are suppressed by coordination of pyridine to the boron atom, with the resulting moiety acting as a Lewis acid of the boroxine component. The pyridine-coordinated nanotube is transformed into a helical coil by humidification. Guest release during the nanotube-to-helical-coil transformation is much slower than during the nanotube-to-sheet transformation, but faster than from a nanotube that did not undergo morphological transformation. The storage and release of guest molecules from the boroxine nanotubes can be precisely controlled by adjusting the moisture level and the concentration of Lewis bases, such as amines.

1. Introduction

Well-designed low-molecular-weight compounds self-assemble in solvents to form supramolecular nanostructures, which also become soft materials such as gels and liquid crystals based on the hierarchization of the supramolecular nanostructures. Compared to covalently bonded polymers and inorganic

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supramolecular nanonanostructures, structures are advantageous because their morphology, size, and dimensions can be finely and quickly re-tuned by use of external stimuli to induce structural changes.^[1] As a result, we are able to control and switch not only the chemical properties of the supramolecular nanostructures but also their physical properties.

Supramolecular nanotubes, which are formed by self-assembly of well-designed amphiphilic molecules in solvents, can act as open-ended nanocapsules for encapsulation of molecules (e.g., drugs and dyes), macromolecules (e.g., DNA and proteins), and nanoparticles.^[2] However, controlling the release of such encapsulated guest molecules from the hollow cvlinder of the nanotube to bulk media is challenging. Morphological transformation of the nanotubes via external stimuli should strongly influence guest release. Nanotube-to-nanosphere and nanotubeto-nanofiber transitions, as well as transitions of nanotubes into nanotubes

with different inner diameters, have already been achieved by environmental changes such as changes in pH,^[3] salt concentration,^[3] temperature,^[4] dilution,^[5] solvation,^[6] and complexation, or by specific reactions of components in the nanotubes with additives such as metals,^[7] cyclodextrin,^[8] poly(propylene glycol),^[9] and enzymes.^[10] Furthermore, we recently developed photoresponsive nanotubes that are able to instantly release guests as the tubular structures shrink and unfold in response to ultraviolet-visible (UV/vis) irradiation.[11]

Herein we investigate the self-assembly behavior of various boroxines (Scheme 1) to form constructed nanotubes, whose morphology can be tuned by hydrolyzing the boroxine molecules to boronic acid. We describe the controlled release of guest molecules through moisture-stimulated morphological transformations from nanotube to sheet, and from nanotube to helical coil.

2. Self-Assembly Behavior/Morphological **Transformation of Nanotubes**

Boroxines ((R-BO)₃), which are formed by dehydration of boronic acids $(R-B(OH)_2, R = alkyl, aryl)$, have an exclusively

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six-membered ring, regardless of the nature of the substituent (R).^[12] The persistence of the six-membered ring is attributable to the resonance stabilization of the conjugated six π -electron



system. Boroxines have received attention owing to their promise as advanced functional materials for two-dimensional covalent organic frameworks (COFs), which are formed by dehydration of $R-B(OH)_2$ ($R = C_6H_4Br$, $C_6H_4B(OH)_2$, and so on).^[13] COFs are of great interest for gas storage, chemical reactors, nanopatterning, and opto-electronics. On the other hand, systematic studies of the self-assembled structures of boroxines (R = aromatic ring without substituted groups, as shown in Scheme 1), which never form COFs, have scarcely been performed until now.

We carried out self-assembly experiments by refluxing the boroxines (1 mg) in toluene (1 mL) for 1 h. The hot solutions were gradually cooled to room temperature. Scanning electron microscopy (SEM) observations revealed that the boroxines independently formed nanofibers 10-20 nm wide and several tens of micrometers in length (R = 2- and 3-thienyl), nanorods 50–400 nm wide and with sub-micrometer lengths (R = phenyl, 3-biphenyl, and 4-biphenyl), and nanotapes 50-100 nm wide and several tens of micrometers in length (R = 1- and 2-naphtyl, 2- and 9-anthracenyl) (Figure 1). All the self-assemblies shown in Figure 2 had no hollow structures, whereas a self-assembly formed from boroxine (R = pyrenyl, abbreviated as (Py-BO)₃ hereafter) had well-defined open ends in its fibers (Figure 2a). Transmission electron microscopy (TEM) observation clearly displays a hollow cylinder, indicating that the self-assembled morphology was tubular (Figure 2b). The nanotubes had uniform inner diameters of ~8 nm and a membrane thickness of ~4 nm.



Figure 1. SEM images of the self-assemblies formed from boroxines ((R–BO)₃, R = various aromatic rings) in toluene: (a,b) nanofibers, (c–e) nanorods, and (f–i) nanotapes.





Figure 2. (a) SEM image of nanotubes self-assembled from $(Py-BO)_3$. (b) TEM image of nanotubes self-assembled from $(Py-BO)_3$ (c) SEM image of sheets formed by the humidity-induced morphological transformation of nanotubes (relative humidity 55%). (d) SEM image of helical coils formed by humidity-induced morphological transformation of pyridine-coordinated nanotubes (relative humidity 55%).

Boroxines easily evolve into their corresponding boronic acids via hydrolysis reactions (Scheme 1). We expected such hydrolysis reactions to alter the morphologies of the boroxine self-assemblies. We stored the nanotubes self-assembled from (Py–BO)₃ in a desiccator, in which the humidity was precisely controlled by saturated aqueous solutions of salts. This humid environment induced a morphological transformation from nanotube to sheet structures (Figure 2c), through an unzipping process^[6b] of the nanotube (Supporting Information, Figure S1). Infrared spectroscopy for the sheet showed the O–H stretching vibration band at 3235 cm⁻¹,

corresponding to 1-pyrenylboronic acid (Py– B(OH)₂) (**Figure 3**a), suggesting that the hydrolysis of the boroxine is closely related to this morphological transformation. The time dependence for the absorbance of the O–H stretching vibration band provided information about the rate of boroxine hydrolysis, which depended strongly on the humidity (Figure 3b).

UV–vis spectroscopic measurements were carried out to analyze the molecular packing in the nanotube and sheet. The absorption band ($\lambda_{max} = 429$ nm) of the nanotube self-assembled from (Py–BO)₃ showed a bathochromic shift compared with that ($\lambda_{max} = 357$ nm) of (Py–BO)₃ that dissolved in toluene (**Figure 4**a), indicating that (Py–BO)₃ forms *J*-type aggregates in the nanotube (**Figure 5**b). On the other hand, the absorption band ($\lambda_{max} = 302$ nm) of the sheet composed of Py–B(OH)₂, which was formed

by hydrolysis of $(Py-BO)_3$ in the nanotube, showed a hypsochromic shift compared with that ($\lambda_{max} = 347$ nm) of Py-B(OH)₂ dissolved in toluene (Figure 4b). These results indicated that the boronic acid forms *H*-type aggregates in the sheet (Figure 5a). Thus, the morphological transformation from nanotube to sheet was caused not only by the structural change from boroxine to the boronic acid, but also by the rearrangement of the molecular packing from *J*-type to *H*-type aggregation.

3. Moisture-Responsive Guest Release

We expected that the humidity-induced morphological transformation from nanotube to sheet would strongly influence the release behavior of pre-encapsulated guests in the nanotubes' hollow cylinders. Figure 6 shows the release profile of *cis*-jasmone (a flavor component of jasmine essential oil) as a guest molecule. Under low relative humidity (6%), which strictly inhibits the hydrolysis of the boroxine as shown in Figure 3b, slow

release of the encapsulated *cis*-jasmone into the bulk media was observed. Such slow release can be ascribed to the nanotubes' high axial ratio.^[14] Further humidification promoted the release of the *cis*-jasmone (Figure 6 and Supporting Information, Figure S2), as a result of the morphological transformation from nanotube to sheet. The rapid release rate observed here was found to correspond to the hydrolysis rate of the boroxine in the nanotube (Figure 3b). The complete release of the *cis*-jasmone was clearly related to the time required for the complete hydrolysis of the boroxine (compare the blue data points



Figure 3. (a) IR spectral change induced by the hydrolysis of $(Py-BO)_3$ in nanotubes under 55% humidity for 2 days. (b) Changes in the IR absorbance at 3235 cm⁻¹ upon the hydrolysis of $(Py-BO)_3$ in nanotubes under different humidity conditions. (c) Changes in the IR absorbance at 3235 cm⁻¹ upon the hydrolysis of $(Py-BO)_3$ in pyridine-coordinated nanotubes under different humidity conditions.





Figure 4. (a) Absorption spectra of $(Py-BO)_3$ in nanotubes dispersed in toluene at 25 °C and of $(Py-BO)_3$ dissolved in toluene without aggregation at 100 °C. (b) Absorption spectra of $Py-B(OH)_2$ in sheets dispersed in toluene at 25 °C and of $Py-B(OH)_2$ dissolved in toluene without aggregation at 100 °C. (c) Absorption spectra of nanotubes and helical coils dispersed in toluene at 25 °C. Absorbance of each spectrum appears to be normalized.

in Figure 6 with the blue data points in Figure 3b). The sheet may have no cavity for storing *cis*-jasmone, as we expected from the observed fast release of the guest molecules (**Figure 7**).

4. Amine- and Moisture-Responsive Guest Release

Boron in boronic acids, boronate esters, and boroxines has been known to act as a hard Lewis acid and can bind bases and



Figure 5. (a) Schematic image of the *H*-aggregate of $Py-B(OH)_2$ in a sheet. (b) Schematic image of the *J*-aggregate of $(Py-BO)_3$ in nanotubes and helical coils.

anions; such binding is accompanied by a molecular orbital change from sp² to sp^{3[15]} and increases the boronate esters' and boroxines' stability against hydrolysis. We investigated the effects of bases, pyridine and ammonia, on the hydrolysis of the boroxine nanotubes, their morphological transformation, and their release of guest molecules.



Figure 6. Release profile of *cis*-jasmone encapsulated in the hollow cylinders of nanotubes with and without morphological transformations.





Figure 7. (a) Schematic illustration of guest release from a sheet, a nanotube, and a helical coil.

Pyridine (3.5 mg, 44.2 µmol) was dropped onto dried nanotubes (10.0 mg, 14.6 µmol), and then the nanotubes were washed with cyclohexane to remove any unbound pyridine. The unbound pyridine in cyclohexane was determined by UV-vis spectroscopy. The number of pyridine molecules coordinated to each boron atom in the boroxine was estimated to be 0.6-0.9, which is reflective of a 1:1 complex formed between the boroxine (R = phenyl) and pyridine.^[16] Although the *I*-aggregate of the nanotubes was slightly changed upon coordination with pyridine, as observed from the slight UV-vis spectral change (Figure 4c), the nanotubes never exhibited any morphological changes. However, humidification of the pyridine-coordinated nanotubes induced a morphological transformation from nanotubes to helical coils with 10 nm width (Figure 2d). IR also indicated that the pyridine-coordinated boroxine had undergone hydrolysis; however, the degree of hydrolysis, i.e., the enhancement of the O-H stretching vibration band, was remarkably smaller than that observed for the above system without pyridine (Figures 3b and 3c). Since the J-aggregate structure was clearly maintained after the morphological transformation from nanotube to helical coil (Figure 4c), we concluded that the coordinated pyridine contributed to suppressing boroxine hydrolysis and boronic acid formation.

The release of *cis*-jasmone associated with the morphological transformation from nanotube to helical coil (squares in Figure 6) was slower than that associated with the morphological transformation from nanotube to sheet (circles in Figure 6); suggests that the helical coil had a hollow cylinder to store *cis*jasmone. On the other hand, the faster release from the helical coil (squares in Figure 6) compared with the release from the nanotubes (triangles in Figure 6) suggests that the release from the helical coil occurs not only from both open ends, as is observed for the nanotubes, but also at the interstices of the helical coils (Figure 7). In lieu of coordination with pyridine, ammonia, which is volatized from 28% NH₃ aqueous solution, also allowed unmodified nanotubes to transform into helical coils and actively released *cis*-jasmone (Supporting Information, Figures S3 and S4).

5. Conclusions

We have constructed nanotubes by self-assembly of $(Py-BO)_3$ in toluene without specific chemical modifications. Humidification of the nanotubes and coordination with amines induced nanotube-to-sheet and nanotube-to-helical coil transitions, respectively. Those morphological transformations enabled precise control of guest molecule release from the nanotubes. These unique properties of the boroxine nanotubes have never been reported for other boron-based materials.^[13,17] The results of the present study could facilitate the development of advanced supramolecular nanocapsules for analytical, biological, medical, cosmetic, and other practical applications.

6. Experimental Section

Synthesis of Boroxines: Boronic acids were refluxed in toluene in the presence of molecular sieves (4\AA) for 1 h. After the solvent was evaporated, the obtained residues were recrystallized from chloroform for several times. The products, formed as powders, were stored in a vacuum desiccator.

Boroxine (R = 2-thienyl). MALDI-TOF mass (m/z): [M + H]⁺ calculated for C₁₂H₁₀B₃O₃S₃: 331.01; found: 331.87. Elemental analysis: Calcd. (%): C, 43.70; H, 2.75. Found: C, 43.72; H, 2.73.

Boroxine (R = 3-thienyl). MALDI-TOF mass (m/z): [M + H]⁺ calculated for C₁₂H₁₀B₃O₃S₃: 331.01; found: 331.84. Elemental analysis: Calcd. (%): C, 43.70; H, 2.75. Found: C, 43.75; H, 2.79.

Boroxine (R = phenyl). MALDI-TOF mass (m/z): [M + H]⁺ calculated for C₁₈H₁₅B₃O₃: 313.14; found: 313.86. Elemental analysis: Calcd. (%): C, 69.35; H, 4.85. Found: C, 69.30; H, 4.81.

Boroxine (R = 3-biphenyl). MALDI-TOF mass (m/z): $[M + H]^+$ calculated for $C_{36}H_{28}B_3O_3$: 541.03; found: 541.22. Elemental analysis: Calcd. (%): C, 80.07; H, 5.04. Found: C, 80.15; H, 5.12.

Boroxine (R = 4-biphenyl). MALDI-TOF mass (m/z): $[M + H]^+$ calculated for C₃₆H₂₈B₃O₃: 541.03; found: 541.25. Elemental analysis: Calcd. (%): C, 80.07; H, 5.04. Found: C, 80.19; H, 5.15.

Boroxine (R = 1-naphthyl). MALDI-TOF mass (m/z): $[M + H]^+$ calculated for C₃₀H₂₂B₃O₃: 463.19; found: 463.36. Elemental analysis: Calcd. (%): C, 78.01; H, 4.58. Found: C, 77.98; H, 4.50.

Boroxine (R = 2-naphthyl). MALDI-TOF mass (m/z): $[M + H]^+$ calculated for C₃₀H₂₂B₃O₃: 463.19; found: 463.54. Elemental analysis: Calcd. (%): C, 78.01; H, 4.58. Found: C, 77.99; H, 4.51.

Boroxine (R = 2-anthracenyl). MALDI-TOF mass (m/z): $[M + H]^+$ calculated for C₄₂H₂₈B₃O₃: 613.23; found: 612.23. Elemental analysis: Calcd. (%): C, 82.41; H, 4.45. Found: C, 82.47; H, 4.49.

Boroxine (R = 9-anthracenyl). MALDI-TOF mass (m/z): $[M + H]^+$ calculated for C₄₂H₂₈B₃O₃: 613.23; found: 612.25. Elemental analysis: Calcd. (%): C, 82.41; H, 4.45. Found: C, 82.49; H, 4.50.



Boroxine (R = pyrenyl). MALDI-TOF mass (m/z): $[M + H]^+$ calculated for C₄₈H₂₈B₃O₃: 684.22; found: 684.10. Elemental analysis: Calcd. (%): C, 84.27; H, 3.98. Found: C, 84.33; H, 3.42.

SEM and TEM Observations: The self-assemblies were dropped onto carbon grids and dried under vacuum. The SEM (Hitachi S-4800) and TEM (Hitachi H-7000) instruments were operated at 30 and 75 keV, respectively.

Fourier Transform-IR and UV-vis Spectroscopic Measurements: IR spectra of the self-assemblies were measured with a Fourier transform IR spectrometer (JASCO FT-620) operated at 4 cm⁻¹ resolution with an unpolarized beam and an attenuated total reflection accessory system (Diamond MIRacle, horizontal ATR accessory with a diamond crystal prism, Pike Technologies, USA) and a mercury cadmium telluride detector. UV-vis spectra of the self-assemblies and of *cis*-jasmone were measured with a spectrophotometer (Hitachi U-3300) equipped with a temperature controller (Yamato BU150A).

Preparation of Nanotubes Encapsulating cis-Jasmone: A toluene solution (5 mL) of cis-jasmone (24.0 mg, 146 µmol) was dropped onto dried boroxine nanotubes (10.0 mg, 14.6 µmol). Capillary action enabled the nanotubes to encapsulate *cis*-jasmone. After aging overnight in a refrigerator, the solution was filtered through a polycarbonate membrane with 0.2 μ m pore size. The residual nanotubes were washed several times with toluene to remove any unencapsulated *cis*-jasmone. The amount of encapsulated *cis*-jasmone was determined as follows: the nanotubes were transformed to sheet in the presence of water, thereby the encapsulated *cis*-jasmone was compulsively released. The released cis-jasmone was selectively extracted into cyclohexane, and the UV-vis spectrum of the solution was measured. The amount of encapsulated cis-jasmone in the nanotubes (5.0 mg) was calculated to be 0.30-0.35 mg.

Release Experiments: Nanotubes encapsulating cis-jasmone were placed into the desiccator, in which the humidity was precisely controlled. Relative humidities of 6%, 32%, 55%, and 86% were achieved by keeping saturated aqueous solutions of NaOH, CaCl₂/6H₂O, Ca(NO₃)₂, and KCl, respectively, in the desiccator. After certain time, the amount of residual cis-jasmone in the nanotubes was determined by UV/vis spectroscopic measurements as described above. The release ratio was calculated from the concentration of the residual *cis*-jasmone and the initial concentration of the encapsulated *cis*-jasmone.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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