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# Chain length dependent alkane/ $\beta$ -cyclodextrin nonamphiphilic supramolecular building blocks†

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In this work we report the chain length dependent behavior of the nonamphiphilic supramolecular building blocks based on the host–guest inclusion complexes of alkanes and  $\beta$ -cyclodextrins ( $\beta$ -CD). <sup>1</sup>H NMR, ESI-MS, and SAXS measurements verified that upon increasing the chain length of alkanes, the building blocks for vesicle formation changed from channel type 2alkane@2 $\beta$ -CD via channel type alkane@2 $\beta$ -CD to non-channel type 2alkane@2 $\beta$ -CD. FT-IR and TGA experiments indicated that hydrogen bonding is the extensive driving force for vesicle formation. It revealed that water molecules are involved in vesicle formation in the form of structural water. Upon changing the chain length, the average number of water molecules associated with per building block is about 16–21, depending on the chain length.

## Introduction

Molecular self-assembly, a ubiquitous process in chemistry, biology, and materials science, provides the foundation for building a variety of nanostructures.<sup>1–6</sup> Among the various structures, vesicles have always been considered as one of the most important types owing to their promising applications in fields such as drug<sup>7</sup> and gene delivery<sup>8</sup> and nanoreactors.<sup>9</sup> To meet the different application demands, extensive efforts have been made to design various building blocks to fabricate functional vesicles.<sup>9–13</sup> Amphiphiles have been verified to be a large family of building blocks to form vesicles, such as surfactants,<sup>14</sup> lipid molecules,<sup>15</sup> polymers<sup>8,16</sup> and aromatic organic compounds.<sup>17,18</sup> In the last two decades, nonamphiphiles such as polyoxometalate macroions<sup>19–22</sup> have also been found to be effective building blocks for vesicle formation. The amphiphilic molecules self-assemble into vesicles driven by the hydrophobic effect and mediated by a hydrophobic–hydrophilic balance.<sup>23</sup> In contrast, the driving forces for nonamphiphilic vesicles can be electrostatic interactions, van der Waals interactions and hydrogen bonding *etc.*<sup>19,24</sup> With superiorities in some aspects over their amphiphilic counterparts, such as better environmental adaptiveness, versatile functionalities, enhanced biocompatibility, *etc.*, nonamphiphiles as a new class of building blocks are attracting considerable attention.<sup>19,24,25</sup> However, so far the

fabrication of proper nonamphiphilic building blocks for the formation of vesicles and other self-assembled structures still remains challenging.

Recently, nonamphiphilic building blocks based on the host–guest inclusion complexes of cyclodextrins (CDs) and surfactants have been developed in our lab.<sup>23,26–31</sup> CDs are doughnut-like oligosaccharides with a hydrophilic exterior and a hydrophobic cavity.<sup>32</sup> The hydrophobic cavity is an ideal harbor in which poorly water-soluble molecules can shelter their hydrophobic parts.<sup>33</sup> Therefore, upon addition of surfactants into the aqueous solution of CD, nonamphiphilic building blocks can be formed if the whole hydrophobic tail of surfactants was included into the cavity of CD. Our group revealed that when  $\beta$ -CD and surfactants, such as sodium dodecyl sulphate (SDS)<sup>23,29</sup> or Tween 20,<sup>30</sup> complex at the molar ratio of 2 : 1, the resultant surfactant@2 $\beta$ -CD inclusion complexes can self-assemble into vesicles, tubes, and lamellar structures simply with increasing concentration. These self-assemblies are predominantly driven by hydrogen bonding between  $\beta$ -CDs,<sup>29,30</sup> which demonstrates that the nonamphiphilic building block surfactant@2 $\beta$ -CD has been fabricated. Most surprisingly, our latest work shows that other than surfactants, dodecane can also form a 2 : 1 inclusion complex with  $\beta$ -CD, which further self-assembles into vesicles or bricks depending on concentrations.<sup>34</sup> Meanwhile, Hao *et al.* revealed that nonamphiphilic vesicles can be constructed by the 1 : 1 host–guest complexes formed with  $\beta$ -CD and small aromatic molecules.<sup>35</sup> These results strongly indicate that different alkanes may produce different nonamphiphilic building blocks with  $\beta$ -CD. Therefore, it is highly desired to carry out a systematic study to verify this conclusion.

Herein we show that the chain length of alkanes has a great influence on the structure of nonamphiphilic building blocks formed with  $\beta$ -CD. In the case of short chained alkanes with

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5 to 10 carbons, the building block is channel type 2alkane@2 $\beta$ -CD, which can be looked on as the dimer of alkane@ $\beta$ -CD. Upon increasing the chain length to 12–14 carbons, the building blocks take the form of alkane@2 $\beta$ -CD. Interestingly, upon further increasing the chain length to 16 and 18 carbons, the building block changes back to the form of 2alkane@2 $\beta$ -CD but with non-channel type arrangement of  $\beta$ -CD. All these nonamphiphilic building blocks self-assemble into unilamellar and bilamellar vesicles in dilute solutions. Our results revealed for the first time that variation of the chain length has significant effects on the fundamental structure of the nonamphiphilic building blocks, which brings new perspectives in designing self-assembled structures.

## Experimental section

### Materials

*n*-Pentane and *n*-hexane were purchased from Beijing Chemical Works. *n*-Tetradecane, *n*-hexadecane and *n*-octadecane were purchased from Alfa Aesar. *n*-Octane, *n*-decane and  $\beta$ -cyclodextrin ( $\beta$ -CD) with a water content of 14% were purchased from Sino-pharm Chemical Reagent Co. Ultrapure water was used throughout the experiment.

### Sample preparation

For the precipitated samples, alkane was added into the  $\beta$ -CD solutions of 16 mM and then the samples were vortex mixed sufficiently to create the white precipitates. After removing the supernatant, the alkane/ $\beta$ -CD precipitates were lyophilized for further measurements. Since the solubility of alkane/ $\beta$ -CD complexes is about 2 mM, vesicular samples were prepared by weighting desired amounts of lyophilized alkane/ $\beta$ -CD precipitates into test tubes followed by addition of water to give the alkane/ $\beta$ -CD concentration of 2 mM. The resultant solutions were thermostatically incubated at 25 °C (for at least 24 h) to allow self-assembly formation.

### Dynamic light scattering (DLS)

Dynamic light scattering (DLS) measurements were conducted on an ALV/DLS/SLS5022F light scattering-apparatus, equipped with a 22 mW He–Ne laser (632.8 nm wavelength) with a refractive index matching bath of filtered toluene surrounding the cylindrical scattering cell. The samples were filtered by 450 nm filters. The scattering angle was set from 30° to 90°.

### TEM observation

The morphology of the self-assemblies was observed using a JEM-100CX II transmission electron microscope (JEOL, Japan). A drop of the sample was placed on 230 mesh copper grids coated with Formvar film. Excess water was removed with filter paper followed by staining the film negatively with uranyl acetate. After the removal of the excess staining liquid by filter paper, the samples were placed at room temperature to dry for TEM observation.

### Atomic force microscopy (AFM)

AFM measurements in tapping mode under ambient conditions were conducted on a D3100 AFM (VEECO, USA). One drop of the alkane/ $\beta$ -CD solution was spin-coated on a mica surface, and then placed at room temperature to dry before AFM observation.

### Fourier transform infrared (FT-IR)

FT-IR measurements were performed on a Nicolet Magna IR 750 equipped with an infrared microspectrograph (Thermo Scientific Co., USA). The vesicle samples were frozen in liquid nitrogen and subsequently lyophilized for 48 h before FT-IR measurements.

### <sup>1</sup>H NMR measurements

The lyophilized alkane/ $\beta$ -CD precipitates were dissolved into DMSO-*d*<sub>6</sub> for <sup>1</sup>H NMR measurements to determine the actual ratio of alkane to  $\beta$ -CD. The measurements were performed on an AVANCE III 500 MHz NMR (Bruker, Switzerland). All the proton signals were calibrated with the TMS at 0.00 ppm. By comparing the integration between  $\beta$ -CD (H1 protons,  $\delta$  4.83 ppm) and the total proton integration of alkanes, the alkane/ $\beta$ -CD complex ratio can be determined.

### ESI-MS measurements

ESI-MS measurements were carried out on an APEX IV FT-MS (Bruker, USA). The operating conditions of the ESI source: positive ion mode; spray voltage –3300 V; capillary voltage –3800 V, capillary temperature 230 °C; skimmer1 33.0 V, skimmer2 28.0 V; sheath gas nitrogen pressure 0.3 bar. The 1 mM alkane/ $\beta$ -CD vesicle samples were diluted 10 times by methanol and introduced *via* direct infusion at a flow rate of 3.00  $\mu$ L min<sup>–1</sup>.

### SAXS measurements

SAXS measurement of the  $\beta$ -CD powder and lyophilized alkane/ $\beta$ -CD precipitates was conducted on a high-flux small-angle X-ray scattering instrument (SAXSess, Anton Paar) equipped with a Kratky blockcollimation system. A Philips PW3830 sealed-tube X-ray generator (Cu K $\alpha$ ) was employed to simultaneously measure the small-angle and wide-angle X-ray scattering (WAXS and SAXS) of the samples. The scanning patterns extend to the high-angle range (the  $q$  range covered by the imaging plate is from 0.0 to 27.2 nm<sup>–1</sup>,  $q = 4\pi \sin \theta/\lambda$ , where  $\lambda$  is the wavelength of 0.1542 nm and  $2\theta$  is the scattering angle). The scattering angles were calibrated with aluminum.

### TGA and DSC measurements

TGA and DSC measurements were conducted synchronously on a Q600SDT (Thermal Analysis Company, USA). The vesicle samples were frozen in a liquid nitrogen bath followed by a vacuum freeze drying step before TGA and DSC measurements. The lyophilized samples were placed into the alumina crucible

with air as the reference. The heating-rate was  $2 \text{ K min}^{-1}$  from 20 to  $120 \text{ }^\circ\text{C}$ .

## Results and discussion

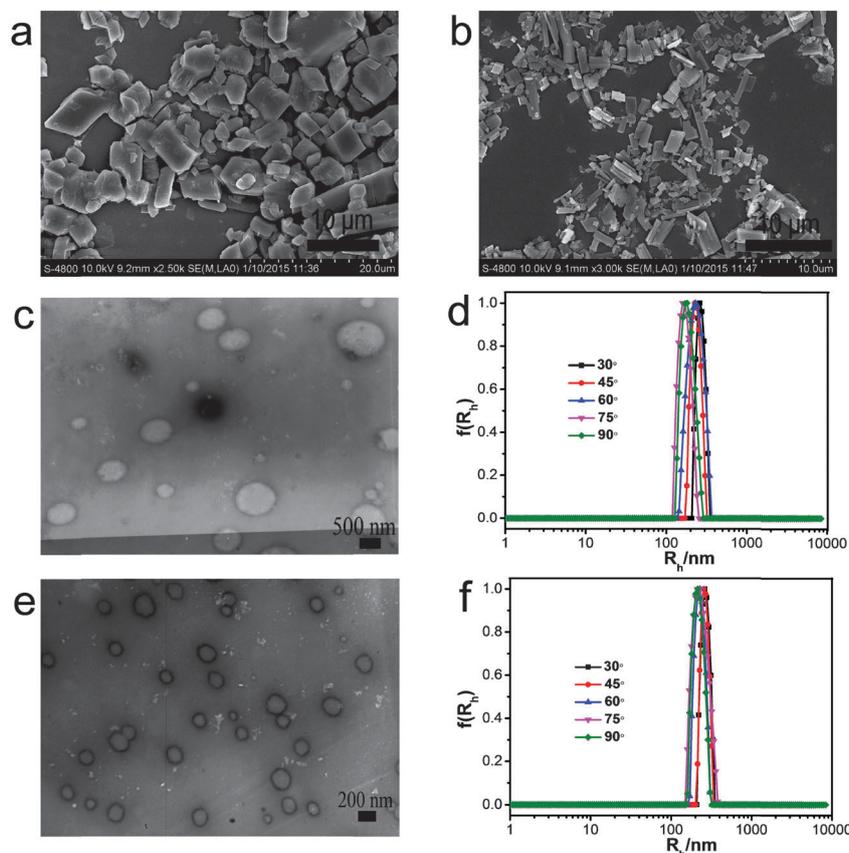
### General information about the formation of alkane/ $\beta$ -CD inclusion complexes

Upon the addition of excess alkanes with chain lengths ranging from 5 to 18 carbons into the transparent solution of 16 mM  $\beta$ -CD, white precipitates occurred immediately, indicating the formation of alkane/ $\beta$ -CD complexes.<sup>36,37</sup> As further evidence, the precipitates were collected and freeze-dried. Then they were redispersed in DMSO- $d_6$  for  $^1\text{H}$  NMR measurements (Fig. S1, ESI $^\dagger$ ).<sup>38</sup> All the proton signals were assigned to  $\beta$ -CD and alkane, and the host-guest molar ratios between them were calculated by comparing the integrations of  $\beta$ -CD (H1 protons) with the total integrations of alkane protons.<sup>39</sup> As shown in Table 1, for the alkane with a shorter carbon chain (from pentane to decane), the host:guest ratio of 1:1 was found for the precipitates. As the chain length increases to 12 and 14 carbons, the molar ratio between  $\beta$ -CD and alkane was changed to 2:1. (The dodecane@ $2\beta$ -CD complexes have been reported in our previous work.<sup>34</sup>) As the chain length of the alkane is further increased to 16 or 18 carbons,

**Table 1** The host-guest ratio of alkane/ $\beta$ -CD complexes attained according to  $^1\text{H}$  NMR results. (The  $^1\text{H}$  NMR spectra were given in Fig. S1)

Alkane	Host-guest ratio
Pentane	1:1
Hexane	1:1
Octane	1:1
Decane	1:1
Dodecane	2:1
Tetradecane	2:1
Hexadecane	1:1
Octadecane	1:1

the  $\beta$ -CD:alkane complexing ratio becomes 1:1 again. Furthermore, ESI-MS measurements were employed to detect the detailed structural information of the building blocks. It was found that the supramolecular structures in all the 1:1 systems are  $2\text{alkane}@2\beta\text{-CD}$ . For instance, ESI-MS measurement of the hexane/ $\beta$ -CD sample shows the presence of  $[2\text{hexane}@2\beta\text{-CD}-5\text{H}_2\text{O} + 3\text{H}]^{3+}$  ( $m/z = 784.89421$ , the theoretical value  $m/z = 784.97754$ ) (Fig. S2a, ESI $^\dagger$ ). In Fig. S2b (ESI $^\dagger$ ), the octadecane/ $\beta$ -CD system shows the presence of  $[2(2\text{octadecane}@2\beta\text{-CD})-6\text{H}_2\text{O} + 2\text{Na}]^{2+}$  ( $m/z = 2747.26566$ , the theoretical value  $m/z = 2747.29566$ ). However, the ESI-MS results of our previous work show that the supramolecular unit in the dodecane/ $\beta$ -CD system is dodecane@ $2\beta$ -CD.<sup>34</sup> This means that the chain length of the alkanes has



**Fig. 1** SEM micrographs of (a) hexane/ $\beta$ -CD precipitates and (b) octadecane/ $\beta$ -CD precipitates. TEM micrograph of (c) the hexane/ $\beta$ -CD sample ( $C_{\text{hexane}@\beta\text{-CD}} = 2 \text{ mM}$ ) and (e) octadecane/ $\beta$ -CD sample ( $C_{\text{octadecane}@\beta\text{-CD}} = 2 \text{ mM}$ ). DLS results at varying scattering angles of (d) the hexane/ $\beta$ -CD ( $C_{\text{hexane}@\beta\text{-CD}} = 2 \text{ mM}$ ) and (f) octadecane/ $\beta$ -CD sample ( $C_{\text{octadecane}@\beta\text{-CD}} = 2 \text{ mM}$ ).

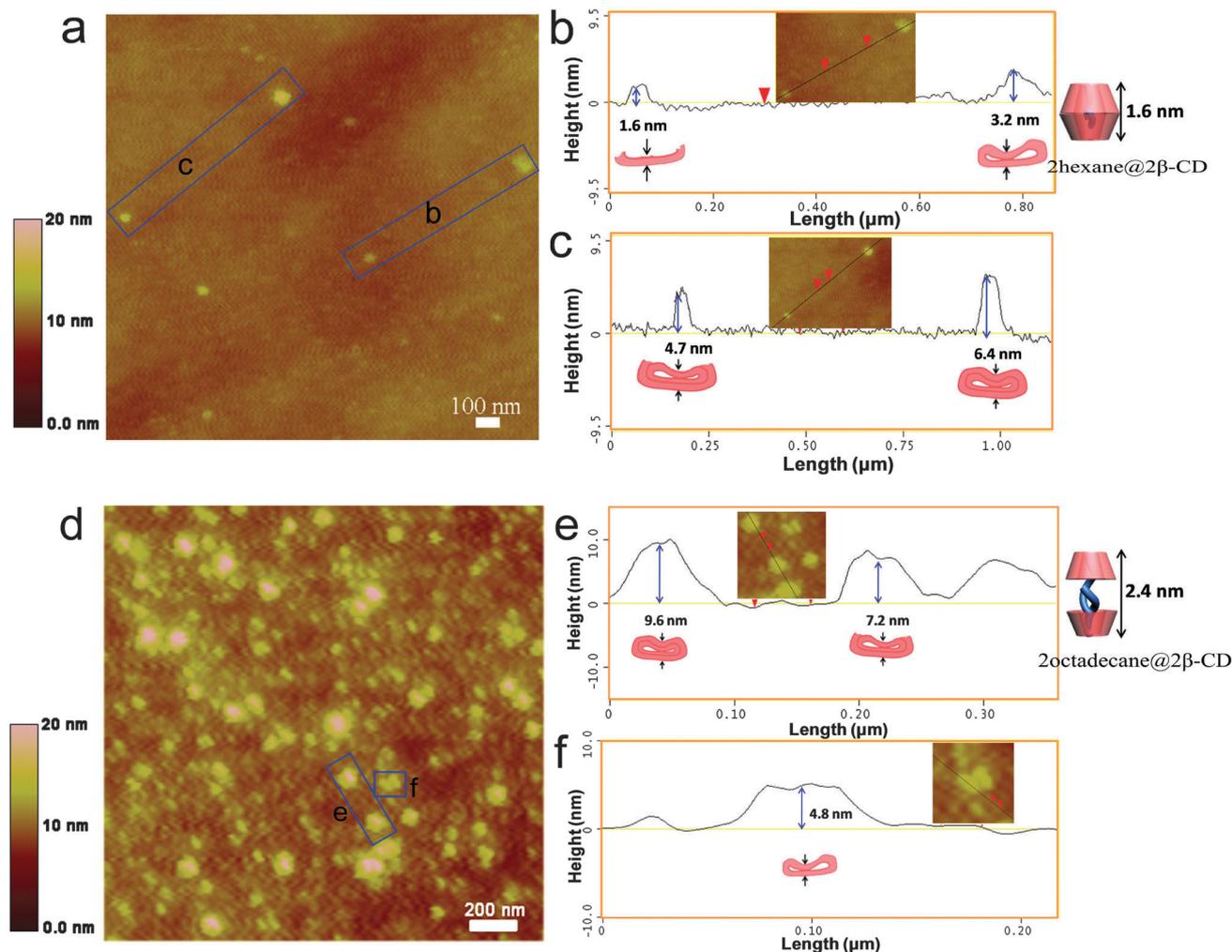


Fig. 2 Images acquired by AFM for vesicles of (a) hexane/ $\beta$ -CD ( $C_{\text{hexane}@\beta\text{-CD}} = 2$  mM) and (d) octadecane/ $\beta$ -CD ( $C_{\text{octadecane}@\beta\text{-CD}} = 2$  mM) sample. (b and c) Are the sectional height profiles of a collapsed unilamellar/bilamellar vesicle and the corresponding broken ones in (a). (e and f) The sectional height profiles of vesicles in (d). The drawings in (b) and (e) are the illustrations of the supramolecular building blocks for 2hexane@2 $\beta$ -CD and 2octadecane@2 $\beta$ -CD, respectively.

distinct effects on the structure of the supramolecular building block. In the following we study in detail the short and long-chained systems, respectively, each taking a representative example.

### Self-assembled structures formed with various building blocks

Self-assembled structures were formed in all these alkane/ $\beta$ -CD inclusion systems. Here we will take the hexane and octadecane systems to demonstrate the self-assembling behaviors in systems with short (with 5 to 10 carbons) and long-chained alkanes (with 16 and 18 carbons), respectively.

At high concentrations, the self-assembly has resulted in precipitates due to the formation of micrometer sized particles (Fig. 1a and b). However, at low concentrations, precipitation can be avoided and vesicles are found. It is noticed that although 'brick-like' particles with parallelogram appearance were formed in both systems, the size of the 'bricks' in the hexane/ $\beta$ -CD system is larger than that in the octadecane/ $\beta$ -CD system. Similar size differences were also found for the vesicles. In Fig. 1c–f we show the TEM and DLS measurements of the

vesicles in hexane/ $\beta$ -CD and octadecane/ $\beta$ -CD, respectively. It is found that the TEM image of the 2 mM hexane/ $\beta$ -CD sample contains vesicles with diameters of 100–500 nm (Fig. 1c). Meanwhile, angle-dependent DLS measurements (Fig. 1d) also revealed the presence of spherical structures with an average hydrodynamic radius of about 200–300 nm, in line with the particle size observed under TEM. In contrast, the TEM image in Fig. 1e suggests that the vesicles in the octadecane/ $\beta$ -CD system are with an average radius of about 100 nm, and the size distribution is much narrower. Angle-dependent DLS measurements verified that the size of the vesicles changes only slightly with variation of the detecting angle (Fig. 1f), confirming the presence of narrowly dispersed spherical structures.

In order to probe the effect of chain length, AFM measurements were performed to get the information of the building blocks. The AFM images in Fig. 2a reveal the presence of polydispersed disks with the diameters of 50–100 nm in the hexane/ $\beta$ -CD system. This size is smaller than the particle size observed by TEM and DLS, which is attributed to the loss

of the larger particles caused by spin-coating during AFM sample preparation. In Fig. 2b we show the sectional height profile of two disks, where the heights of the inmost recesses are  $\sim 3.2$  nm and 1.6 nm, respectively. Considering that both the height of one  $\beta$ -CD and the extending length of hexane are about 0.8 nm, the height of 1:1 complexed hexane@ $\beta$ -CD should be 0.8 nm as well since the chain of hexane can be completely buried in the cavity of  $\beta$ -CD. However, we have known from ESI-MS results that the basic building block in this system is 2hexane@2 $\beta$ -CD (the illustration in Fig. 2b). Therefore, the height of 3.2 nm corresponds to a collapsed unilamellar vesicle, whereas 1.6 nm is probably the height of a broken vesicle, as demonstrated in Fig. 2b. In addition, we also observed in Fig. 2c that the height of two disks is about 6.4 nm and 4.7 nm, which were considered as a collapsed and a broken bilamellar vesicle, respectively.

The AFM images of the vesicles formed in the octadecane/ $\beta$ -CD systems are given in Fig. 2d–f. Fig. 2d verifies the presence of the hollow vesicular structures with a height to diameter ratio of about 1 : 10. Fig. 2e shows the sectional height profile of two disks, in which the lowest heights are  $\sim 9.6$  nm and 7.2 nm, respectively. Considering that the height of one  $\beta$ -CD and the extending length of octadecane are about 0.8 and 2.3 nm, respectively, the height of 1:1 octadecane@ $\beta$ -CD complexes is expected to be 2.3 nm. However, the height difference between 7.2 nm and 9.6 nm indicates that the length of the basic building block in this system should be  $9.6 - 7.2 = 2.4$  nm, which equals to the summation of the height of  $\beta$ -CD and octadecane. In combination with the ESI-MS result which demonstrates the presence of the 2octadecane@2 $\beta$ -CD unit, we inferred that two octadecane@ $\beta$ -CD complexes form the dimer-typed building block with a strong interdigitation of the chain of octadecane *via* hydrophobic interaction, as illustrated in Fig. 2e.<sup>40,41</sup> Therefore, the two disks with the height of 9.6 nm and 7.2 nm were thought to be a collapsed and a broken bilamellar vesicle, respectively. Consequently, the disk with the height of 4.8 nm in Fig. 2f can be considered as a collapsed unilamellar vesicle.

It is amazing that the octadecane/ $\beta$ -CD complexes are in the form of 2octadecane@2 $\beta$ -CD, rather than octadecane@ $\beta$ -CD. One would have expected that the 1:1 inclusion complex of octadecane/ $\beta$ -CD should be in the form of the latter, which is a supraamphiphile.<sup>42–45</sup> In that case, it would display surface active properties. However, the surface tension of the 2 mM octadecane/ $\beta$ -CD aqueous solution, which is the saturate solution of the inclusion complex, was found to be  $71.9 \text{ mN m}^{-1}$  at  $25^\circ\text{C}$ . This surface tension is nearly the same as that of pure water, verifying the absence of the amphiphilic structure of octadecane@ $\beta$ -CD.<sup>37</sup> Instead, it suggests that 2octadecane@2 $\beta$ -CD is nonamphiphilic.

Obviously, although the building blocks in both the short chained (represented by hexane/ $\beta$ -CD) and long chained (represented by octadecane/ $\beta$ -CD) systems are in the same form of 2alkane@2 $\beta$ -CD, their structures are different. This difference can be revealed by SAXS measurements. It is well-known that two possible crystalline structures, namely, cage-type and channel-type, can be formed through  $\beta$ -CD/guest inclusion complexes.<sup>46,47</sup> In Fig. 3, we show the SAXS pattern of the lyophilized hexane/ $\beta$ -CD,

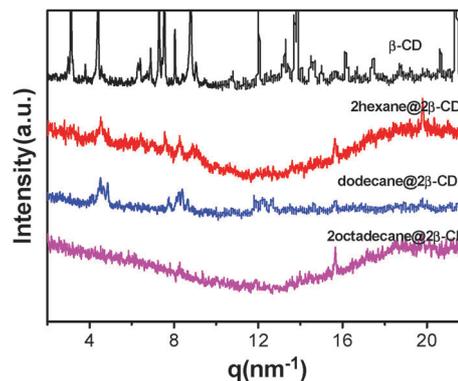


Fig. 3 The SAXS spectrum of  $\beta$ -CD powder and the lyophilized alkane (hexane, dodecane, octadecane)/ $\beta$ -CD precipitates.

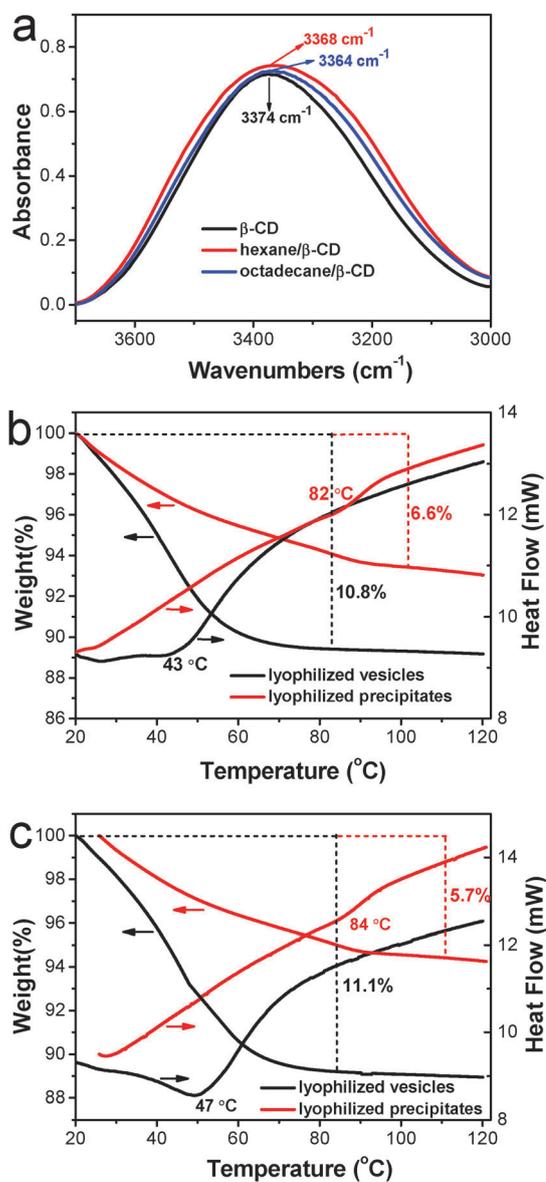
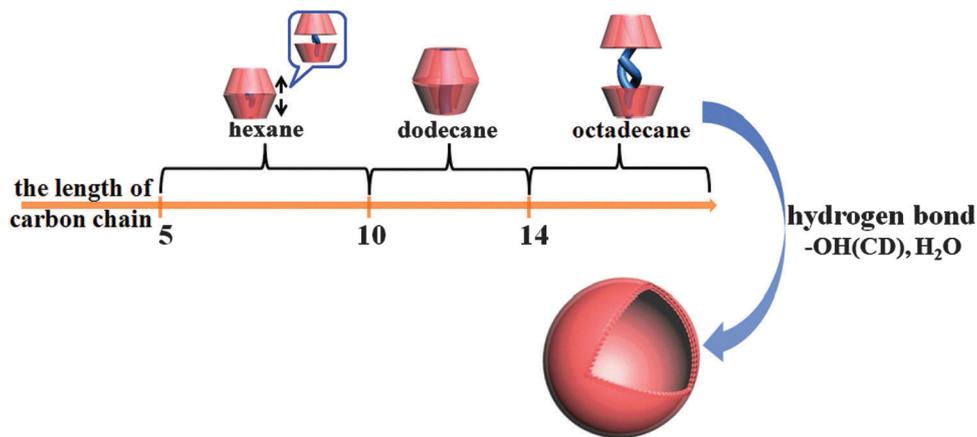


Fig. 4 (a) FT-IR spectra of  $\beta$ -CD powder, the lyophilized hexane/ $\beta$ -CD vesicles and octadecane/ $\beta$ -CD vesicles. (b and c) TGA and DSC results of the lyophilized hexane/ $\beta$ -CD and octadecane/ $\beta$ -CD samples, respectively.



Scheme 1 A schematic of the self-assembly behavior of alkane/ $\beta$ -CD building blocks.

which is dramatically different from that of cage-type  $\beta$ -CD powders, but similar to the channel-type structures of dodecane@2 $\beta$ -CD which is featured by the presence of a peak at  $q = 8.2$  and  $12.4 \text{ nm}^{-1}$ .<sup>34</sup> In contrast, the octadecane/ $\beta$ -CD complexes did not show the characteristic peaks of channel-type or cage-type, suggesting that there are no  $\beta$ -CD arrays in the vesicles. This is in line with our expectation: the interdigitated octadecane chains between two  $\beta$ -CDs have separated the two  $\beta$ -CD units in the form of 2octadecane@2 $\beta$ -CD.

#### Role of hydrogen bonding and water in the vesicles

Since both the building blocks are nonamphiphilic, hydrogen bonding should play an essential role in the vesicle formation. This can be verified by the urea addition experiments. As urea was added into the vesicular suspension, the vesicles were found disassembled (Fig. S3, ESI†). Since urea is an excellent hydrogen bonding agent, it competes the hydrogen bond formation with CD. Therefore, the disassembly of vesicles in the presence of urea indicates that hydrogen bonding is indeed the driving force for vesicle formation. Furthermore, the presence of hydrogen bonding was further proved in the FT-IR experiments. The hydroxyl band for the powder of  $\beta$ -CD occurs at  $3374 \text{ cm}^{-1}$  (Fig. 4a), whereas that for the lyophilized vesicles moved to a lower wavenumber of  $3368$  and  $3364 \text{ cm}^{-1}$  in the 2hexane@2 $\beta$ -CD and 2octadecane@2 $\beta$ -CD system, respectively, demonstrating the formation of hydrogen bonds.<sup>48</sup>

The hydrogen bonds that drive the vesicle formation may be formed solely between CDs, or mediated by water. To clarify this point, TGA and DSC experiments were performed. The lyophilized vesicles show weight losses of 10.8% at  $43^\circ\text{C}$  for the 2hexane@2 $\beta$ -CD system and 11.1% at  $47^\circ\text{C}$  for 2octadecane@2 $\beta$ -CD, respectively (Fig. 4b and c). This considerable amount of water can be attributed to those structurally bonded to the hydroxyl groups of  $\beta$ -CD in the vesicle membrane.<sup>49</sup> In contrast, the structural water in the lyophilized brick-like precipitates (Fig. 1a and b) is only 6.6% and 5.6% for these two systems which occurred at a much higher temperature of about  $82^\circ\text{C}$ . It is striking that the content of water in the precipitates is much less than that in the vesicles, suggesting that the structural water is

very crucial for the vesicle formation. According to the data obtained from the TGA, the number of water molecules around one 2hexane@2 $\beta$ -CD and 2octadecane@2 $\beta$ -CD in the vesicles is about 16  $[(10.8/18.0)/(89.2/2442.32) = 16.4]$  and 19  $[(11.1/18)/(88.9/2778.96) = 19.3]$ , respectively, which have mediated the formation of vesicles. In contrast, this number of water molecules in the dodecane@2 $\beta$ -CD vesicle is 21.<sup>34</sup> This chain length dependent number of water molecules in vesicles indicates that the hydrogen bond driven self-assembling system has a strong ability of self-adjustment.

## Conclusion

In summary, we reported the effect of the chain length of alkanes on the formation of nonamphiphilic building blocks with  $\beta$ -cyclodextrin in this work. Upon variation of the chain length of alkanes, different building blocks can be obtained. For short chained alkanes with 5 to 10 carbons, the building block is channel-type 2alkane@2 $\beta$ -CD. Upon increasing the chain length to 12–14 carbons, the building blocks take the channel-type form of alkane@2 $\beta$ -CD. Upon further increasing the chain length to 16 and 18 carbons, the building block changes back to the form of 2alkane@2 $\beta$ -CD but with the non-channel type. Driven by the hydrogen bond between  $\text{H}_2\text{O}$  and the hydroxyl groups of  $\beta$ -CD, these nonamphiphilic building blocks can self-assemble into unilamellar and bilamellar vesicles in dilute solutions (Scheme 1). It is anticipated that the chain length dependent behavior of nonamphiphilic building blocks would shed light on the elegant control of the nonamphiphilic self-assembled structures.

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## Notes and references

- 1 G. M. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418–2421.
- 2 A. C. Coleman, J. M. Beierle, M. C. Stuart, B. Maciá, G. Caroli, J. T. Mika, D. J. van Dijken, J. Chen, W. R. Browne and B. L. Feringa, *Nat. Nanotechnol.*, 2011, **6**, 547–552.
- 3 C. Wang, Z. Wang and X. Zhang, *Small*, 2011, **7**, 1379–1383.
- 4 H. Yang, Q. An, W. Zhu, W. Li, Y. Jiang, J. Cui, X. Zhang and G. Li, *Chem. Commun.*, 2012, **48**, 10633–10635.
- 5 J. Bae, J.-H. Choi, Y.-S. Yoo, N.-K. Oh, B.-S. Kim and M. Lee, *J. Am. Chem. Soc.*, 2005, **127**, 9668–9669.
- 6 T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev.*, 2005, **105**, 1401–1444.
- 7 T. M. Allen and P. R. Cullis, *Science*, 2004, **303**, 1818–1822.
- 8 O. Onaca, R. Enea, D. W. Hughes and W. Meier, *Macromol. Biosci.*, 2009, **9**, 129–139.
- 9 P. Tanner, P. Baumann, R. Enea, O. Onaca, C. Palivan and W. Meier, *Acc. Chem. Res.*, 2011, **44**, 1039–1049.
- 10 J. Du and R. K. O'Reilly, *Soft Matter*, 2009, **5**, 3544–3561.
- 11 J. Voskuhl and B. J. Ravoo, *Chem. Soc. Rev.*, 2009, **38**, 495–505.
- 12 F. Versluis, I. Tomatsu, S. Kehr, C. Fregonese, A. W. Tepper, M. C. Stuart, B. J. Ravoo, R. I. Koning and A. Kros, *J. Am. Chem. Soc.*, 2009, **131**, 13186–13187.
- 13 T. Sun, Q. Guo, C. Zhang, J. Hao, P. Xing, J. Su, S. Li, A. Hao and G. Liu, *Langmuir*, 2012, **28**, 8625–8636.
- 14 C. Wu, Y. Hou, M. Deng, X. Huang, D. Yu, J. Xiang, Y. Liu, Z. Li and Y. Wang, *Langmuir*, 2010, **26**, 7922–7927.
- 15 S.-L. Huang and R. C. MacDonald, *Biochim. Biophys. Acta, Biomembr.*, 2004, **1665**, 134–141.
- 16 F. Ahmed and D. E. Discher, *J. Controlled Release*, 2004, **96**, 37–53.
- 17 Y.-X. Xu, G.-T. Wang, X. Zhao, X.-K. Jiang and Z.-T. Li, *Langmuir*, 2009, **25**, 2684–2688.
- 18 F. J. Hoeben, I. O. Shklyarevskiy, M. J. Pouderoijen, H. Engelkamp, A. P. Schenning, P. Christianen, J. C. Maan and E. Meijer, *Angew. Chem.*, 2006, **118**, 1254–1258.
- 19 T. Liu, E. Diemann, H. Li, A. W. Dress and A. Müller, *Nature*, 2003, **426**, 59–62.
- 20 G. Liu, T. Liu, S. S. Mal and U. Kortz, *J. Am. Chem. Soc.*, 2006, **128**, 10103–10110.
- 21 T. Liu, B. Imber, E. Diemann, G. Liu, K. Cokleski, H. Li, Z. Chen and A. Müller, *J. Am. Chem. Soc.*, 2006, **128**, 15914–15920.
- 22 M. L. Kistler, A. Bhatt, G. Liu, D. Casa and T. Liu, *J. Am. Chem. Soc.*, 2007, **129**, 6453–6460.
- 23 L. Jiang, Y. Peng, Y. Yan and J. Huang, *Soft Matter*, 2011, **7**, 1726–1731.
- 24 D. Li, J. Zhang, K. Landskron and T. Liu, *J. Am. Chem. Soc.*, 2008, **130**, 4226–4227.
- 25 L. Wu, J. Lal, K. A. Simon, E. A. Burton and Y.-Y. Luk, *J. Am. Chem. Soc.*, 2009, **131**, 7430–7443.
- 26 L. Jiang, Y. Yan and J. Huang, *Adv. Colloid Interface Sci.*, 2011, **169**, 13–25.
- 27 Y. Yan, L. Jiang and J. Huang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9074–9082.
- 28 L. Jiang, Y. Yan and J. Huang, *Soft Matter*, 2011, **7**, 10417–10423.
- 29 L. Jiang, Y. Peng, Y. Yan, M. Deng, Y. Wang and J. Huang, *Soft Matter*, 2010, **6**, 1731–1736.
- 30 C. Zhou, X. Cheng, Q. Zhao, Y. Yan, J. Wang and J. Huang, *Langmuir*, 2013, **29**, 13175–13182.
- 31 C. Zhou, X. Cheng, Y. Yan, J. Wang and J. Huang, *Langmuir*, 2014, **30**, 3381–3386.
- 32 J. Szejtli, *Chem. Rev.*, 1998, **98**, 1743–1754.
- 33 E. Junquera, G. Tardajos and E. Aicart, *Langmuir*, 1993, **9**, 1213–1219.
- 34 C. Zhou, X. Cheng, Q. Zhao, Y. Yan, J. Wang and J. Huang, *Sci. Rep.*, 2014, **4**, 7533.
- 35 S. Li, L. Zhang, B. Wang, M. Ma, P. Xing, X. Chu, Y. Zhang and A. Hao, *Soft Matter*, 2015, **11**, 1767–1777.
- 36 I. Sanemasa, Y. Wu, Y. Koide, M. Shigenaga, K. Ishibashi and T. Deguchi, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1424–1429.
- 37 Z. P. Dou, H. Xing and J. X. Xiao, *Chem. – Eur. J.*, 2011, **17**, 5373–5380.
- 38 H.-J. Schneider, F. Hacket, V. Rüdiger and H. Ikeda, *Chem. Rev.*, 1998, **98**, 1755–1786.
- 39 W. Tao, Y. Liu, B. Jiang, S. Yu, W. Huang, Y. Zhou and D. Yan, *J. Am. Chem. Soc.*, 2011, **134**, 762–764.
- 40 J. H. Jung, G. John, K. Yoshida and T. Shimizu, *J. Am. Chem. Soc.*, 2002, **124**, 10674–10675.
- 41 J. H. Jung, Y. Do, Y. A. Lee and T. Shimizu, *Chem. – Eur. J.*, 2005, **11**, 5538–5544.
- 42 X. Zhang and C. Wang, *Chem. Soc. Rev.*, 2011, **40**, 94–101.
- 43 T. Bojinova, Y. Coppel, N. Lauth-de Viguierie, A. Milius, I. Rico-Lattes and A. Lattes, *Langmuir*, 2003, **19**, 5233–5239.
- 44 C. Machut, F. Mouri-Belabdelli, J.-P. Cavrot, A. Sayede and E. Monflier, *Green Chem.*, 2010, **12**, 772–775.
- 45 H. Zhang, W. An, Z. Liu, A. Hao, J. Hao, J. Shen, X. Zhao, H. Sun and L. Sun, *Carbohydr. Res.*, 2010, **345**, 87–96.
- 46 A. Harada, M. Okada, J. Li and M. Kamachi, *Macromolecules*, 1995, **28**, 8406–8411.
- 47 W. Saenger, J. Jacob, K. Gessler, T. Steiner, D. Hoffmann, H. Sanbe, K. Koizumi, S. M. Smith and T. Takaha, *Chem. Rev.*, 1998, **98**, 1787–1802.
- 48 D. Ke, C. Zhan, A. D. Li and J. Yao, *Angew. Chem.*, 2011, **123**, 3799–3803.
- 49 L. E. Cheruzel, M. S. Pometun, M. R. Cecil, M. S. Mashuta, R. J. Wittebort and R. M. Buchanan, *Angew. Chem.*, 2003, **115**, 5610–5613.