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ARTICLE

Mechanically-sensitive hydrogels formed from β-cyclodextrin and an anionic surfactant containing a biphenyl group

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Hydrogels are important soft materials with intriguing properties. By taking advantage of the host–guest interactions and multiple molecular interactions, it is expected that novel hydrogel systems can be formed. This strategy has been implemented here, transparent hydrogels were formed by using a newly-synthesized anionic surfactant, sodium 2-(4-phenylphenoxy)dodecanoate (C_{12}biphNa), and β-cyclodextrin (β-CD) in different proportions and their properties were investigated. Gelation of water occurs at extremely low surfactant concentrations (5 mM for a 1:3 C_{12}biphNa:β-CD system), and a single C_{12}biphNa with its associated β-CDs can trap about 11,000 water molecules on average. In addition, the systems are fragile to mechanical stimulus and thus show mechanical sensitivity. Cryo-TEM reveals that the hydrogels have a microstructure consisting of rigid nanowire-like aggregates (with cross-sectional diameters of about 7~8 nm) locally distributed in a parallel manner in solution. These microstructural features are responsible for the peculiar properties of the hydrogel systems presented. The inclusion complexes formed by C_{12}biphNa and β-CD were investigated using ^{1}H NMR and 2D nuclear overhauser effect spectroscopy and their aggregation state was proposed. This work enriches the connotation of nonamphiphilic self-assembly and provides inspiration for constructing new functional soft materials.

Introduction

Hydrogels exist widely in nature and are important soft materials with intriguing properties. The structure of a hydrogel consists of large amounts of water trapped in macromolecular or supramolecular networks.[1] In recent years, great interest has arisen in hydrogels formed by self-assembly of low molecular weight molecules wherein intermolecular forces dominate the characteristics of the hydrogel.[2–7] Such systems are subsequently very sensitive to environmental stimuli such as pH, thermal or chemical signals.[2, 6, 8–10] The features of these supramolecular gels are inspirational for understanding the behavior of their biological counterparts.

It is well known that surfactants can form various aggregates depending on the intermolecular interactions acting. Under appropriate conditions (suitable molecular geometry, concentration, and ionic strength), entangled thread-like hydrogels that can trap water molecules can also be formed.[10–20] The driving force for these surfactant gelators to aggregate is mainly van der Waals forces stemming from hydrophobic groups. However, the van der Waals forces are relatively weak and directionless. The resulting threadlike micelles are soft building blocks of hydrogels. Thus, gelation of water usually needs a rather high concentration of surfactants.

Cyclodextrin (CD), a cyclic oligomer of glucose, has a hydrophilic surface and a hydrophobic cavity and has also been utilized to construct hydrogel systems.[21–23] The pioneering work carried out by Huang et al. reveals that introducing β-CD into a suitable surfactant system results in the formation of supramolecular complexes that further aggregate into annular ring microtubes,[24–26] vesicle,[9, 25–28] lamellae,[25–27, 29] and fibers[26, 30] via hydrogen-bond-invoked non-amphiphilic assembly.[31–33] These aggregates show more obvious rigidity, providing the possibility of reducing the surfactant concentration for hydrogel formation. Of course implementation of this strategy is related to surfactant structure. Here, a new anionic surfactant containing a biphenyl group, namely, sodium 2-(4-phenylphenoxy)dodecanoate (C_{12}biphNa, Fig. 1), the hydrophobic part of which contains both the biphenyl group and the alkyl chain, is used to construct hydrogel systems with β-CD. It is found that, at suitable molar ratios, the C_{12}biphNa/β-CD system can gel water at remarkably low surfactant and β-CD concentrations, which, to the best of our knowledge, is a rare phenomenon. The hydrogels' properties and aggregate morphology have been investigated and the results may open up new pathways for constructing hydrogels with surfactants.

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Electronic Supplementary Information (ESI) available: synthesis of surfactants, determination of association constant, 2D NOESY spectrum and polarized optical images, Cryo-TEM, Rheology. See DOI: 10.1039/x0xx00000x

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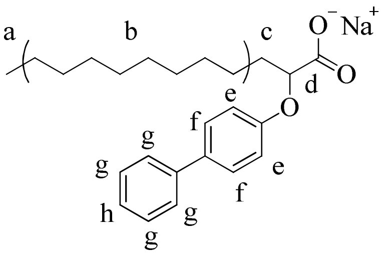

Fig. 1. The molecular structure of C_{12}biphNa.

Experimental

Materials

Dodecanoic acid (purity >98%), ethyl 2-bromoacetate (purity >98%) were purchased from Aladdin Chemistry Company, Ltd.. Thionyl choride, bromine and N,N-Dimethylformamide were analytical grade and were purchased from Sinopharm Chemical Reagent Company, Ltd.. 4-phenylphenol (purity >99%) and sodium laurate (purity > 98%) were purchased from J&K Chemical Company, Ltd.. β-Cyclodextrin (β-CD, purity> 99%) were purchased from Tokyo Chemical Industry Company, Ltd.. Other solvents and reagents were all analytical grade. All of these materials were used without further purification. sodium 2-(4-phenylphenoxy)dodecanoate (C_{12}biphNa) and sodium 2-(4-phenylphenoxy)acetate were synthesized in our laboratory (Supporting Information, Part 1).

Preparation of hydrogels

The mother liquors of C_{12}biphNa and β-CD were first prepared by separately weighing a desired amount of C_{12}biphNa and β-CD into a tube, followed by adding certain volume of water to dissolve. Depending on the concentrations of the samples, different amount of the two mother liquors were weighted and mixed together. The samples were heated to 70 ^{o}C and then kept at 25±0.1 ^{o}C for at least 12 h.

Rheology measurements

Rheological measurements were performed on a stress controlled rheometer (Discovery DHR-2, TA instruments) with cone-plate sensor. The cone is made of standard ETC steel with a diameter of 40 mm and a cone angle of 2°. The gap between the center of cone and the plate is 48 μm. A strain sweep was performed at a frequency of 2.82 rad/s before test. A strain value was then decided to make sure that the sample in the linear viscoelastic region during the following oscillatory measurements. The temperament was kept at 25 ^{o}C throughout the experiments. All the solutions were prepared using Milli-Q water with a resistivity of 18.2 MΩ·cm.

Small-angle X-ray scattering (SAXS)

The C_{12}biphNa:β-CD samples were heated to 70 °C and then injected into capillary tube with a syringe. The sample was kept at 25±0.1 °C for 12h waiting for measurement. Small-angle X-ray scattering (SAXS) measurements were performed using an Anton-Paar SAX Sess mc2 system with Ni-filtered Cu Kα radiation (1.54 Å) operating at 50 kV and 40 mA.

^{1}H–^{1}H 2D NOESY HNMR measurements

C_{12}biphNa, β-CD and D_2O in desired proportion was added into NMR tube. The mixture was gently heated to 70 ^{o}C until the solid was dissolved and it was then kept at 25±0.1 ^{o}C for at least 12h to make sure the formation of gel. 2D NOESY measurement was carried out on a Bruker Aduance Ⅲ 400 spectrometer operating at 400 MHz with the standard three-pulse sequence with a mixing time of 600 ms.

Cryogenic-transmission electron microscopy (Cryo-TEM)

Cryo-TEM samples were prepared in a controlled-environment vitrification system (CEVS). A micropipette was used to load 5 μL of gel onto a TEM copper grid which was blotted with two pieces of filter paper, resulting in the formation of thin films suspended on the mesh holes. Then the gel was quickly plunged into a reservoir of liquid ethane (cooled by nitrogen) at −165 °C. The vitrified samples were then stored in the liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 655) and examined with a JEOL JEM-1400 TEM (120kV) at about −174 °C. The phase contrast was enhanced by the under focus. The images were recorded on a Gatan multiscan CCD and processed with a Digital Micrograph.

Results and discussion

An aqueous solution of C_{12}biphNa remains water-like even at a concentration of 250 mM. Addition of β-CD into surfactant

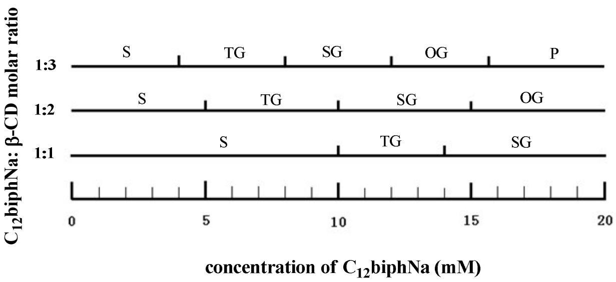

Fig. 2. Phase diagrams for different C_{12}biphNa:β-CD systems at 25 °C. Key: S – solution, TG – transparent gel, SG – semitransparent gel, OG – opaque gel, P – precipitate.

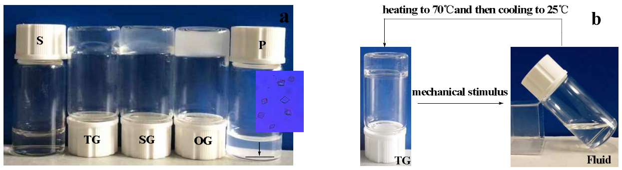

Fig. 3. Illustrations of the 1:3 C_{12}biphNa:β-CD system. (a) Physical appearance at different surfactant concentrations, and (b) the gel–sol transition caused by mechanical stimulus at 5 mM C_{12}biphNa at 25 °C.

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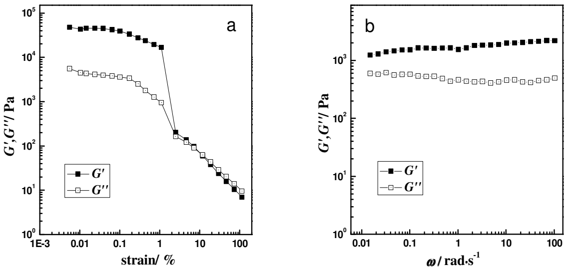

Fig. 4. Variation of G′ (storage symbols) and G′′ (loss symbols) with (a) the percentage strain, and (b) shear frequency, ω, for a 1:3 system of C_{12}biphNa (5 mM) and β-CD at 25 °C.

solutions of low concentration leads to the formation of hydrogels. A simple phase diagram is shown in Fig. 2. Since all the investigated systems show similar phase transition behavior as the surfactant concentration varies, a 1:3 C_{12}biphNa:β-CD system is considered for illustration purposes (Fig. 3).

The system remains fluidic at low surfactant concentrations (<4mM). As concentration increases, transparent hydrogels are formed. Further increasing concentration results in the formation of translucent, and then opaque hydrogels. And precipitates appear when the surfactant concentration is above 15 mM. The precipitate observed using an optical microscope consists of crystalline plates, which is a similar morphology reported in TDPS/β-CD systems.[30] Here, we mainly focus on the transparent gels because they are rather unusual in supramolecular hydrogel systems.

For a 1:3 C_{12}biphNa:β-CD system, the transparent hydrogel formed at a surfactant concentration of 5 mM can hold its own weight in an inverted glass bottle of diameter 2 cm. However, when a mechanical stimulus such as shaking and stirring is applied to the system, the hydrogel transforms to a fluidic liquid (see Fig. 3(b)). This liquid can be restored to the gel state by heating to 70 °C and then cooling to 25 °C. Obviously, a primary feature of the hydrogel system is its mechanical sensitivity, which we further characterized using rheological methods.

As shown in Fig. 4(a), an abrupt decrease in elastic modulus occurs at a strain value of 1%. This means that only a tiny deformation is required to destroy the microstructure of the hydrogel. A strain value of 0.02% was chosen to perform subsequent oscillatory measurements on a fresh sample. As shown in Fig. 4(b). The storage modulus is always greater than the loss modulus, indicative of the elastic nature of the hydrogel. Although many hydrogel systems may share a similar mechanical response,[30] the high mechanical sensitivity of the present system alludes to the high vulnerability of the microstructure within.

Compared with other CD-containing surfactant gel systems, another striking feature of the present systems is that they can gel water at extremely low concentrations. In the system discussed above, for example, the total sum of surfactant and β-CD used is only 1.89% of the total hydrogel weight. A surfactant molecule with its associated β-CD molecules can, on average, trap about 11,000 water molecules. This fact again indicates that the aggregates formed in the hydrogel systems may have unusual morphologies. Cryogenic-transmission electron microscopy (Cryo-TEM) was further used to obtain details of the microstructure of these transparent hydrogels.

As shown in Fig. 5(a) for a 1:1 C_{12}biphNa:β-CD system, long nanowire-like aggregates were observed in the hydrogel. Spherical aggregates with diameters of 10 nm were also found doped among the long nanowires. As the β-CD ratio increases, the nanowire-like aggregates become denser and the lengths of some of the aggregates extend beyond the field of vision. Surprisingly, these aggregates also seem to be arranged, locally, in parallel (this is more obvious in Figs. 5(b) and (c)). This is another microstructural feature of the transparent hydrogel systems.

To further identify the morphology, small-angle X-ray scattering (SAXS) was used to investigate the three samples above. As shown in Fig. 6, sets of Bragg diffraction peaks were observed in the small-angle region in each sample. This implies that periodically-arranged structures occupy the whole of the bulk solution region. The Bragg diffraction patterns shown in Fig. 6 have been suggested as an indication of presence of a lamellar phase in such solutions.[27, 29] However, we have to exclude this interpretation for the following reasons. First, the formation of a lamellar phase usually requires a rather high

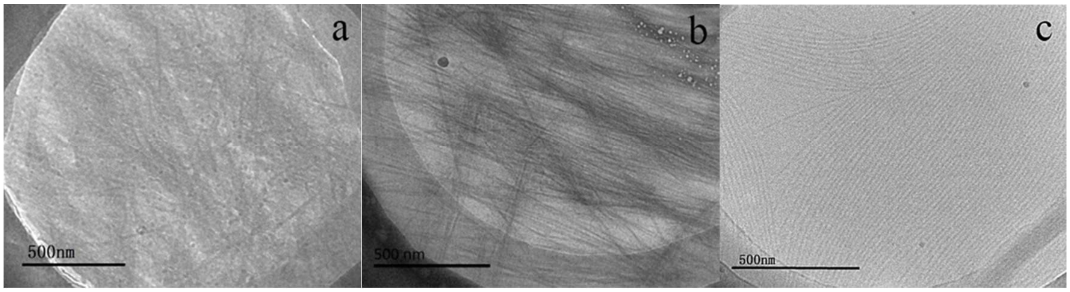

Fig. 5. Cryo-TEM images of (a) a 1:1 system of C_{12}biphNa (10 mM) and β-CD, (b) a 1:2 system of C_{12}biphNa (5 mM) and β-CD and (c) a 1:3 system of C_{12}biphNa (5 mM) and β-CD

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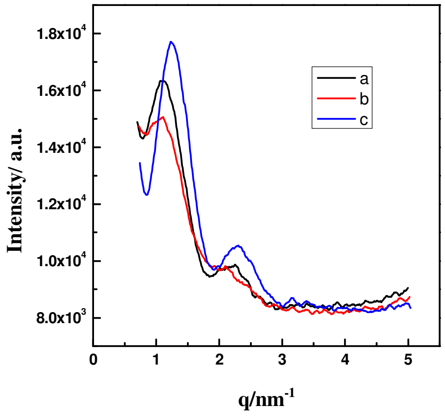

Fig. 6. SAXS profiles of (a) a 1:1 system of C_{12}biphNa (10 mM) and β-CD, (b) a 1:2 system of C_{12}biphNa (5 mM) and β-CD and (c) a 1:3 system of C_{12}biphNa (5 mM) and β-CD

surfactant concentration, whereas the most concentrated solution among the three samples above is at only 10 mM. Second, lamellar phases show birefringence because of their anisotropic nature, but the three samples above all appear dark when observed under a polarizing microscope (Supporting Information, Fig. S8). The Bragg diffraction patterns shown in Fig. 6 are thus the reflection of a locally-parallel arrangement of rigid and long nanowire-like aggregates, verifying the observations made using Cryo-TEM. The distance calculated from the 001 scattering for the investigated three systems is 5.7nm, 5.6nm and 5.1nm respectively, which indicates the cross-sectional diameter of nanowire-like aggregates. Although the diameter obtained from SAXS measurements (5~6nm) is different with Cryo-TEM images (about 7~8nm), it is reasonable when considering that the actual dimeter is only in nano-scale. In the previously reported supramolecular hydrogel systems,[22, 30, 34] the microstructures are entangled fibers or tubes with cross-sectional diameters of several hundred nanometers. In contrast, the present systems feature rigid nanowire-like aggregates with uniform cross-sectional diameters of several nanometers, similar to straightened worm-like micelles. To the best of our knowledge, this novel morphology has never been reported before in CD-containing hydrogel systems. This morphology, which can be formed at extremely low complex concentrations of surfactant and β-CD, is also responsible for the mechanical sensitivity of the hydrogel systems.

The aggregates are formed by inclusion complexes of surfactant and β-CD molecules. The arrangement of these complexes in the aggregates remains a challenging to form the unusual nanowire-like aggregates. Also, C_{12}biphNa contains an alkyl and a biphenyl group and both can associated with β-CD, albeit to different degrees. In order to get a clear picture of the association state between C_{12}biphNa and β-CD, sodium laurate (with a dodecyl alkyl chain) and sodium 2-(4-phenylphenoxy)acetate (with a diphenyl group), were used to separately estimate the stability of the association between the two hydrophobic groups and β-CD.

By using ^{1}H NMR,[35, 36] and assuming a 1:1 stoichiometry (Supporting Information, Part 3), the association constants of sodium laurate and sodium 2-(4-phenylphenoxy)acetate with β-CD were found to be 989.5 M^{-1} and 1705 M^{-1}, respectively. Thus, both groups in C_{12}biphNa, are expected to be associated with β-CD to form stable complexes. However, the diphenyl group has a stronger tendency to form complexes with β-CD than the dodecyl alkyl chain. Moreover, the above three samples were investigated using 2D nuclear Overhauser effect spectroscopy (NOESY). It is known that the cross-peak signals of the protons in a 2D NOESY spectrum indicate a distance between protons of less than 5 Å,[37, 38] which thus provides direct evidence of molecular interaction. For a 1:1 C_{12}biphNa:β-CD system, the 2D NOESY signals (Fig. 7(a)) reveal that the proton in the inner cavity of β-CD interacts with both the alkyl chain and diphenyl ring of the C_{12}biphNa molecule (marked with ellipses and rectangles, respectively). As these signals only appear when an inclusion complex forms, it can be concluded that the two types of complex (dodecyl alkyl chain@β-CD and diphenyl group@β-CD) coexist in the 1:1 C_{12}biphNa:β-CD system. The diphenyl group@β-CD complex appears to be the most abundant one because of its larger association constant. The presence of multiple inclusion complexes may account for the coexistence of spherical and nanowire-like aggregates in the system. In addition, interactions between the alkyl chain and diphenyl ring can also be observed (marked with rhombi in the Fig.7(a)), indicating that part of the unassociated alkyl chain and diphenyl ring are able to keep close to each other in the aggregates.

In a 1:2 C_{12}biphNa:β-CD system, where the amount of β-CD is twice that of C_{12}biphNa, each alkyl chain or diphenyl group has the opportunity to associate with one β-CD, resulting in the formation of the C_{12}biphNa@2β-CD complex. As shown in Fig. 7(b), apart from the interactions belonging to β-CD with the alkyl chain (marked with ellipses) and diphenyl group (marked with rectangles), no signals indicating interactions between the alkyl chain and diphenyl group were observed.

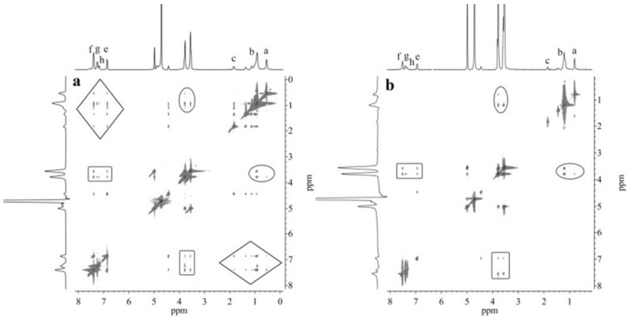

Fig. 7. ^{1}H–^{1}H 2D NOESY spectra of: (a) a 1:1 system of C_{12}biphNa (10 mM) and β-CD, and (b) a 1:2 system of C_{12}biphNa (5 mM) and β-CD.

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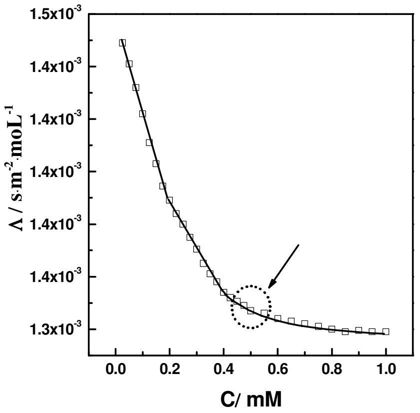

Fig. 8. Variation of the molar conductivity of C_{12}biphNa (0.25 mM) with β-CD concentration at 25 °C.

This means that nearly all the alkyl chains and diphenyl groups in the solution are associated with β-CD, which hinders interaction between the alkyl chain and diphenyl group.

Whether or not a C_{12}biphNa molecule can associate with 3 or more β-CD molecules is unclear because the 2D NOESY spectrum of the 1:3 C_{12}biphNa:β-CD system (Supporting Information Fig. S7) is almost the same as that of the 1:2system. As C_{12}biphNa has multiple association sites, an optimum C_{12}biphNa to β-CD ratio can be expected. Since the diphenyl ring and alkyl chain are unequal groups, the widely used Job's plot is not applicable to the present systems.[39] However, it is known that the formation of complexes between ionic surfactants and CD may result in a decrease of the conductivity of the solutions due to a lower ion-transportation rate correspondingly. Thus conductivity measurements were carried out to roughly estimate the association state between C_{12}biphNa and β-CD.[40] As shown in Fig. 8, the molar conductivity initially sharply decreases as β-CD is added. The break point appears at a β-CD concentration of about 0.5 mM, which coincides with a β-CD:C_{12}biphNa ratio of 2:1. Further addition beyond this ratio sees the molar conductivity decreasing gradually, indicating that complexes of β-CD and C_{12}biphNa with larger stoichiometry are insignificant or absent in the solution.

Combining all the above results, we conclude that C_{12}biphNa@2β-CD complexes are the main building blocks in the hydrogel systems when the ratio of β-CD and C_{12}biphNa is at and above 2:1. The configuration and proposed arrangements of the complexes in the above investigated systems are shown in Fig. 9. The distance between the methyl group of the alkyl chain and the para-position of diphenyl ring was calculated to be 2.5nm for complex a and b. The cross-sectional diameter of the nanowire like aggregate was thus estimated to be 5nm, corresponding well with the values obtained from SAXS experiments. Fig. 9 reveals that the nanowire aggregates have hydrophobic cores along their axes and surfaces covered by β-CD molecules, and the aggregates are formed as a synergistic result of the hydrophobic interactions between the alkyl chains and hydrogen bonds introduced by the β-CD molecules.

It is interesting to know why these nanowire-like aggregates should arrange themselves locally in parallel in the solution. It is generally believed that the building blocks in hydrogel systems initially grow along random directions to form overlapping or entangled structures.[22, 30] We speculate that the formation of this kind of morphology is affected by the temperature used during the preparation of the hydrogel. As the β-CD molecules are destined to located at the surface of these aggregates, the outsides of the aggregates will be covered by hydroxyl groups, which function as one of the driving forces causing aggregate growth through the action of hydrogen bonding. At a high temperature, effects of hydrogen bonding

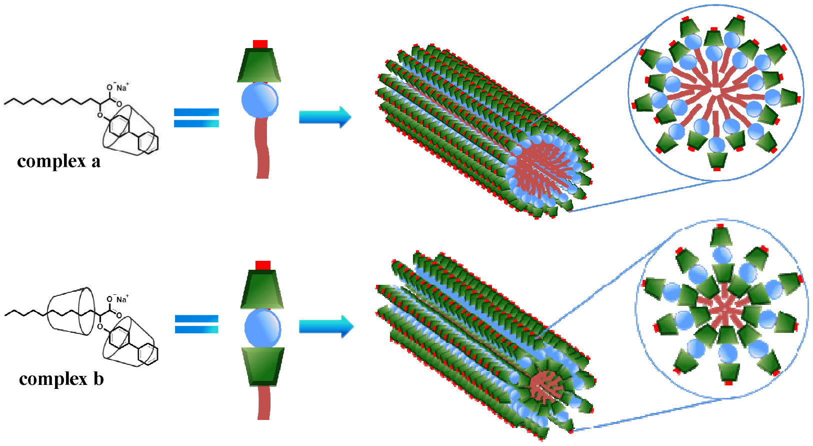

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Fig. 9. Illustrations showing the inclusion complexes in investigated β-CD:C_{12}biphNa systems. Top: a 1:1 system. Bottom: a system in which β-CD:C_{12}biphNa ≥ 2:1. The proposed arrangements inside the aggregates are also shown.

are weak and surface of initially formed aggregates is rather hydrophobic. To reduce the energy of the system, these aggregates tend to move closer to each other to reduce the area of contact with water. Further elongation of aggregates is thus guided by adjacent ones, which leads to the formation of nanowire bundles. With the decrease of temperature, the surface of the nanowire aggregate will recover its hydrophilicity due to the enhancement of the hydrogen bonding effect. Water molecules will then be able to penetrate into the bundles, separating the nanowires more apart from each other on average. These finely dispersed, paralleled nanowires possess large specific surface areas, which is why they can trap large amounts of water molecules.

Conclusions

The formation of hydrogels with mechanical sensitivity has been found in mixed systems consisting of β-CD and a new carboxylate surfactant at several mixing ratios. The C_{12}biphNa /β-CD complexes form rigid nanowire-like aggregates that can gel water with high efficiency. Since the C_{12}biphNa molecule contains an alkyl chain and a biphenyl group, part of the hydrophobic group still remains in the resulted inclusion complex when it associates with β-CD. The synergistic effect of directive hydrogen bonds and hydrophobic interactions among inclusion complexes accounts for the formation of rigid nanowire-like aggregates. The present systems indicate that by taking advantage of novel molecular structures of surfactants, and rationally utilizing the molecular interactions therein, novel aggregate morphologies with unique behavior can be expected. This work enriches the connotation of nonamphiphilic self-assembly and provides inspiration for constructing new functional soft materials in the future.

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References

1 T. Vermonden, R. Censi, and W. E. Hennink, *Chem. Rev.*, 2012, **112**, 2853–2888.…
2 Y. W. Sun and X. R. Huang, *Supramol. Chem.*, 2015, **27**, 21–27.
3 C. Wang, D. Q. Zhang, and D. B. Zhu, *Langmuir*, 2007, **23**, 1478–1482.
4 M. Shirakawa, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, 2005, **127**, 4164–4165.
5 J. Kowalczuk, M. Bielejewski, A. Lapinski, R. Luboradzki, and J. Tritt-Goc, *J. Phys. Chem. B*, 2014, **118**, 4005–4015.
6 T. Taira, Y. Suzaki, and K. Osakada, *Chem. Commun.*, 2009, **45**, 7027–7029.
7 T. Taira, Y. Suzaki, and K. Osakada, *Chem-Eur J.*, 2010, **16**, 6518–6529.
8 Z. L. Chu and Y. J. Feng, *Chem. Commun.*, 2010, **46**, 9028–9030.
9 A. Wang, W. Shi, J. Huang and Y. Yan, *Soft Matter*, 2016, DOI: 10.1039/c5sm02397a.
10 Z. L. Chu and Y. J. Feng, *Chem. Commun.*, 2011, **47**, 7191–7193.
11 H. Hoffmann, *Adv. Mater.*, 1994, **6**, 116–129.
12 R. Kumar, G. C. Kalur, L. Ziserman, D. Danino, and S. R. Raghavan, *Langmuir*, 2007, **23**, 12849–12856.
13 K. Trickett and J. Eastoe, *Adv. Colloid Interface Sci.*, 2008, **144**, 66–74.
14 Y. Y. Lin, Y. Qiao, Y. Yan, and J. B. Huang, *Soft Matter*, 2009, **5**, 3047–3053.
15 Z. W. Yuan, W. J. Lu, W. M. Liu, and J. C. Hao, *Soft Matter*, 2008, **4**, 1639–1644.
16 G. Verma, V. K. Aswal, and P. Hassan, *Soft Matter*, 2009, **5**, 2919–2927.
17 H. Yan, M. W. Zhao, and L. Q. Zheng, *Colloid Surface A*, 2011, **392**, 205–212.
18 D. Wang and J. C. Hao, *Colloid Polym. Sci.*, 2013, **291**, 2935–2946.
19 H. M. Fan, S. Z. Zhao, B. C. Li, H. J. Fan, W. L. Kang, and J. B. Huang, *Rsc Adv.*, 2015, **5**, 27623–27629.
20 Y. M. Hu, L. L. Ge, J. Han, and R. Guo, *Soft Matter*, 2015, **11**, 5624–5631.
21 S. Y. Li, P. Y. Xing, Y. H. Hou, J. S. Yang, X. Z. Yang, B. Wang, and A. Y. Hao, *J. Mol. Liq.*, 2013, **188**, 74–80.
22 J. F. Shi and X. H. Shen, *J. Phys. Chem. B*, 2014, **118**, 1685–1695.
23 J. L. Shen, J. Y. Pang, T. Kalwarczyk, R. Holyst, X. Xin, G. Y. Xu, X. Y. Luan, and Y. J. Yang, *J. Mater. Chem. C*, 2015, **3**, 8104–8113.
24 L. X. Jiang, Y. Peng, Y. Yan, M. L. Deng, Y. L. Wang, and J. B. Huang, *Soft Matter*, 2010, **6**, 1731–1736.
25 L. X. Jiang, Y. Yan and J. B. Huang, *Adv. Colloid Interface Sci.*, 2011, **169**, 13-25.
26 Y. Yan, L. X. Jiang and J. B. Huang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9074-9082.
27 L. X. Jiang, Y. Peng, Y. Yan, and J. B. Huang, *Soft Matter*, 2011, **7**, 1726–1731.
28 B. Jing, X. Chen, X. D. Wang, C. J. Yang, Y. Z. Xie and H. Y. Qiu, *Chem-Eur J*, 2007, **13**, 9137-9142.
29 N. Cheng, Q. Z. Hu, Y. H. Bi, W. W. Xu, Y. J. Gong, and L. Yu, *Langmuir*, 2014, **30**, 9076–9084.
30 L. X. Jiang, Y. Yan, and J. B. Huang, *Soft Matter*, 2011, **7**, 10417–10423.
31 T. B. Liu, E. Diemann, H. L. Li, A. W. M. Dress, and A. Muller, *Nature*, 2003, **426**, 59–62.
32 D. Langevin, *Adv. Colloid Interface Sci.*, 2009, **147–148**, 170–177.
33 L. Wu, J. Lal, K. A. Simon, E. A. Burton, and Y. Y. Luk, *J. Am. Chem. Soc.*, 2009, **131**, 7430–7443.
34 A. Heeres, C. van der Pol, M. C. A. Stuart, A. Friggeri, B. L. Feringa, and J. van Esch, *J. Am. Chem. Soc.*, 2003, **125**, 14252–14253.
35 C. G. Floare, A. Pirnau, and M. Bogdan, *J. Mol. Struct.*, 2013, **1044**, 72–78.
36 H. J. Schneider, F. Hacket, V. Rudiger, and H. Ikeda, *Chem. Rev.*, 1998, **98**, 1755–1785.
37 H. Kessler, M. Gehrke, and C. Griesinger, *Angew. Chem., Int. Ed.*, 1988, **27**, 490–536.
38 Y. X. Fan, Y. B. Hou, J. F. Xiang, D. F. Yu, C. X. Wu, M. Z. Tian, Y. C. Han, and Y. L. Wang, *Langmuir*, 2011, **27**, 10570–10579.
39 L. X. Jiang, M. L. Deng, Y. L. Wang, D. H. Liang, Y. Yan, and J. B. Huang, *J. Phys. Chem. B*, 2009, **113**, 7498–7504.

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40 M. Nilsson, C. Cabaleiro-Lago, A. J. M. Valente, and O. Soderman, *Langmuir*, 2006, **22**, 8663–8669.

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Figures

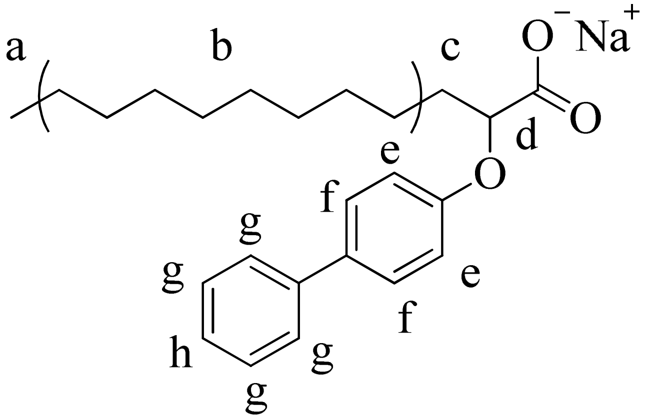

Fig. 1. The molecular structure of C_{12}biphNa.

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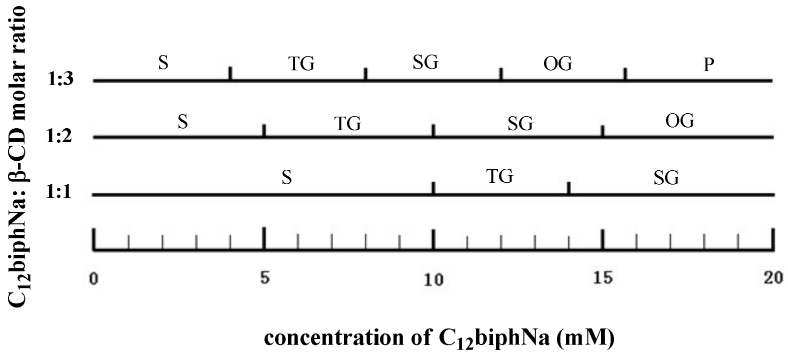

Fig. 2. Phase diagrams for different C_{12}biphNa:β-CD systems at 25 °C. Key: S – solution, TG – transparent gel, SG – semitransparent gel, OG – opaque gel, P – precipitate.

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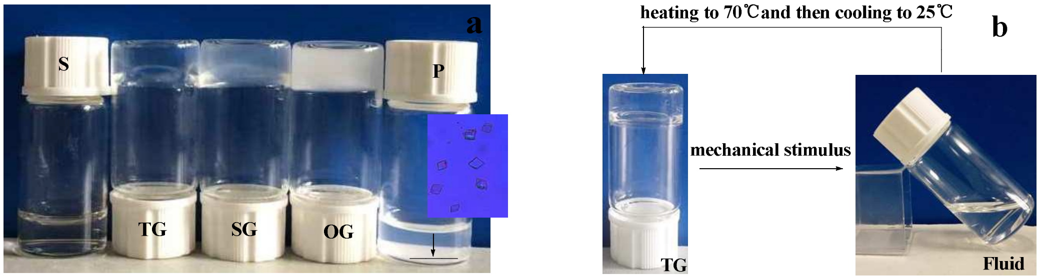

Fig. 3. Illustrations of the 1:3 C_{12}biphNa:β-CD system. (a) Physical appearance at different surfactant concentrations, and (b) the gel–sol transition caused by mechanical stimulus at 5 mM C_{12}biphNa at 25 °C.

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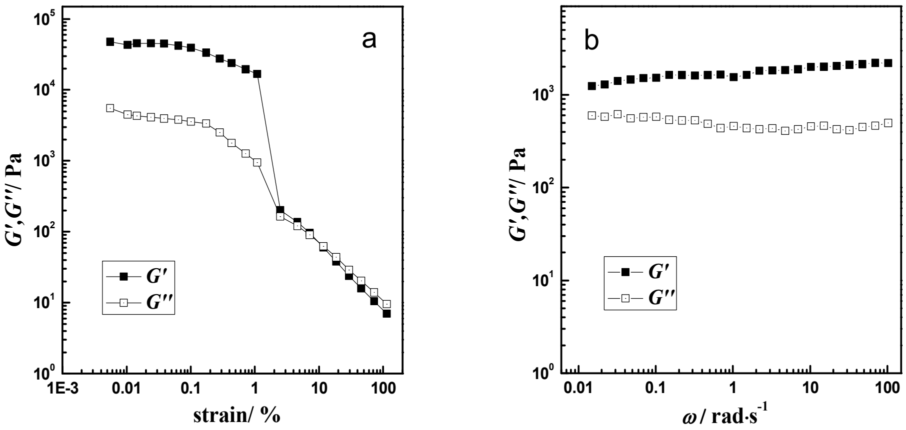

Fig. 4. Variation of G′ (storage symbols) and G″ (loss symbols) with (a) the percentage strain, and (b) shear frequency, ω, for a 1:3 system of C_{12}biphNa (5 mM) and β-CD at 25 °C.

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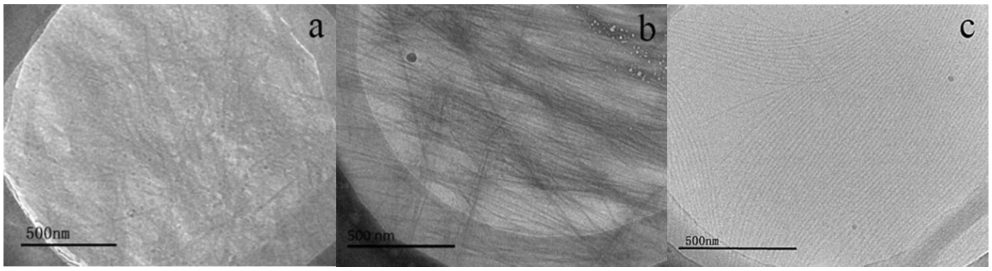

Fig. 5. Cryo-TEM images of (a) a 1:1 system of C_{12}biphNa (10 mM) and β-CD, (b) a 1:2 system of C_{12}biphNa (5 mM) and β-CD and (c) a 1:3 system of C_{12}biphNa (5 mM) and β-CD

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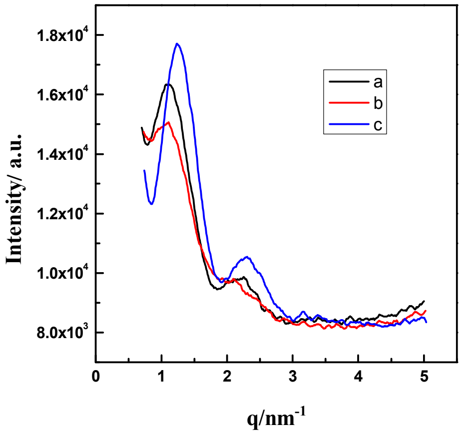

Fig. 6. SAXS profiles of (a) a 1:1 system of C_{12}biphNa (10 mM) and β-CD, (b) a 1:2 system of C_{12}biphNa (5 mM) and β-CD and (c) a 1:3 system of C_{12}biphNa (5 mM) and β-CD

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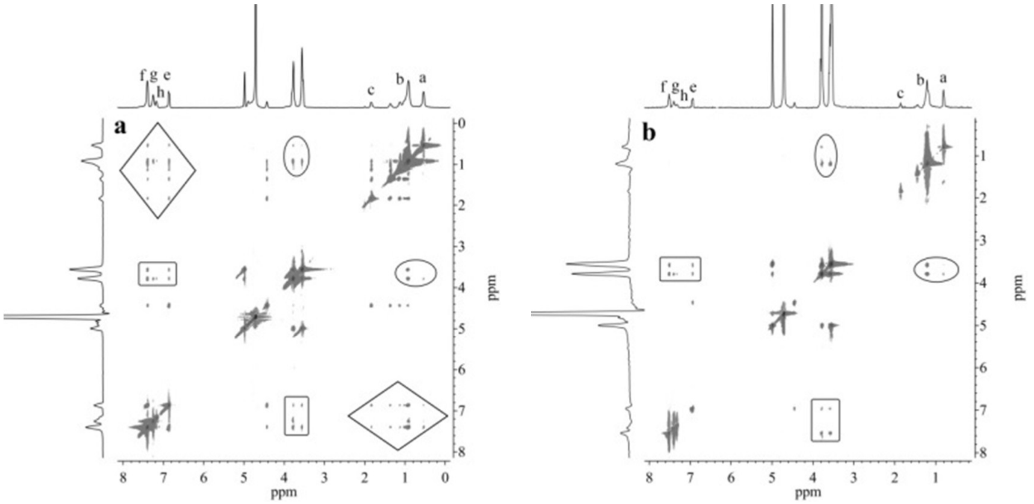

Fig. 7. ^{1}H–^{1}H 2D NOESY spectra of: (a) a 1:1 system of C_{12}biphNa (10 mM) and β-CD, and (b) a 1:2 system of C_{12}biphNa (5 mM) and β-CD.

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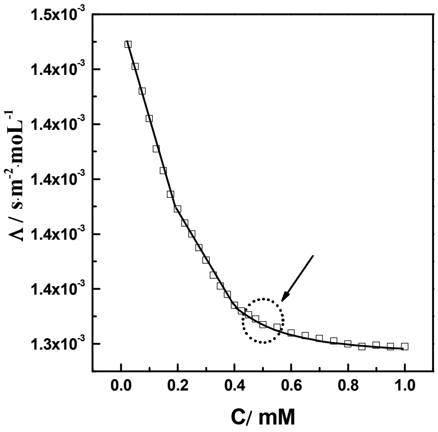

Fig. 8. Variation of the molar conductivity of C_{12}biphNa (0.25 mM) with β-CD concentration at 25 °C.

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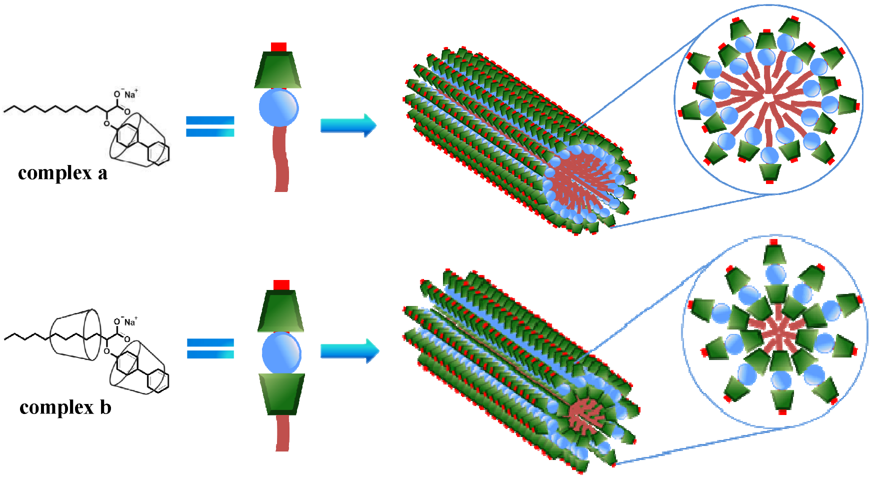

Fig. 9. Illustrations showing the inclusion complexes in investigated β-CD:C$_{12}$biphNa systems. Top: a 1:1 system. Bottom: a system in which β-CD:C$_{12}$biphNa $\geq$ 2:1. The proposed arrangements inside the aggregates are also shown.

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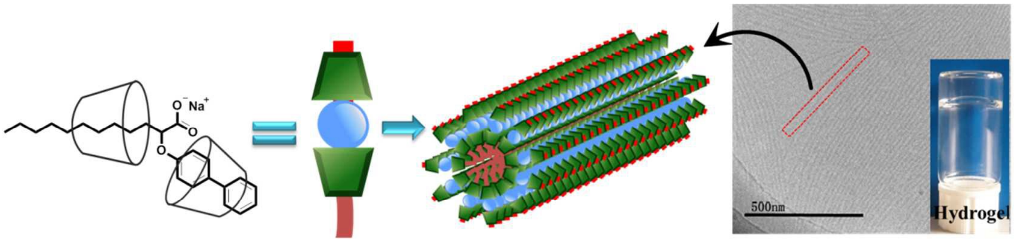
Graphical Abstract



The inclusion complexes formed in an anionic surfactant/β-CD system can self-assemble into rigid nanowires to form hydrogels with mechanical sensitivity.

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