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Self-assembly of supra-amphiphiles building block fabricated by β -cyclodextrin and adamantane-based ionic liquid†

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A new adamantane-based ionic liquid, (11-(((adamantane-1-carbonyloxy)undecyl)-1-methylimidazol-3-ium bromide (AD-C₁₁im), was synthesized from 1-adamantanecarboxylic acid and observed that it can aggregate into micelles in aqueous solution. A number of experiments were conducted to understand the self-assembly of supra-amphiphiles building block fabricated by β -cyclodextrin (β -CD) and adamantane-based ionic liquid at diverse molar ratios. Studies revealed that host-guest interaction between the adamantane group and β -CD occurred and AD-C₁₁im@1 β -CD building block formed when same amount β -CD was added. Then the micelles aggregates formed by AD-C₁₁im only turned into spherical vesicles, which was confirmed by AFM, DLS and TEM. Besides, according to the results of AFM, it can be confirmed that the vesicles were monolayer structure. When double amount β -CD was added, both the adamantane group and the hydrophobic chain were encapsulated by β -CD and AD-C₁₁im@2 β -CD building block formed. Thus the aggregations changed from vesicles to net-like nanofiber, which was observed by TEM. When the β -CD concentration increased to 40 mM, the formation of light blue hydrogel was observed during the self-assembling process of AD-C₁₁im@2 β -CD building block.

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Introduction

Ionic liquids (ILs), which are composed of various ions, have successfully aroused the interest of many scientists during the past few years.¹ Compared with traditional organic solvents, ILs have many unique properties and are widely used in catalysis and chemosynthesis,^{2,3} materials, medicine, energy applications,^{4,5} carbon dioxide capture,^{3,6} analytical applications,⁷ and so on. ILs have been the frontier and hotspots of international green chemistry and chemical industry. Thus, it can provide new ideas to find green medium for chemist and new functional materials for materials scientists.

Recently, supra-amphiphiles serve as building block are fabricated by non-covalent interactions have been developed.⁸ Host-guest interaction, especially based on cyclodextrins (CDs) is an important driving force for super-amphiphilic molecules. It is widely known that CDs are natural molecules and possess a truncated doughnut-shaped structure having hydrophobic inner cavity and hydrophilic surface.⁹ The unique structure of

cyclodextrin results in accommodation of various guest molecules giving rise to the formation of inclusion complexes and these CDs inclusion have been extensively used in separation, analysis, medicine, catalysis and other fields.¹⁰

Both ILs and CDs have special structures and properties and exhibit excellent properties in many areas, such as synthesize, catalysis, separating process and so on. Therefore, the researches on combinations of ILs and CDs are attracting more and more attention. For examples, Amajjahe *et al.* found that [bvim][Tf₂N] exhibited lower critical solution temperature after adding CD and noncomplexed polymer precipitation appeared at higher temperature.¹¹ Han *et al.* studied the inclusion compound of β -CD and bmimPF₆ and discovered that the compound had higher solubility, lower thermal stability and lower decomposition temperature.¹² And they also studied the inclusion complexes of three types of ILs surfactants (C₁₂-mimPF₆, C₁₄mimPF₆ and C₁₆mimPF₆) with β -CD, found the inclusion compound exhibited a channel-type structure and announced the importance of hydrophobicity during the process.¹³ Schmitzer *et al.* used [C₁₂MIM]/[C₁₆MIM] and CD combination for the rhodium-catalyzed hydroformylation reaction of alkenes which not dissolved in water and this created high activity, high regioselectivity and decreased decantation time. This group also demonstrated that the supramolecular compounds formed by CDs and imidazolium salts can be used to alter the first- and the second-coordination sphere of an organometallic predecessor.¹⁴ Roy *et al.* explored inclusion compounds of ILs, 1-butyl-4-methylpyridinium lauryl

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sulfate, with β -CD and revealed the unparalleled configuration of the inclusion compound and they found the concurrence of micelle and vesicle.¹⁵ Shen *et al.* suggested a universal interaction between an IL (C_{12} mimBr) and β -CD and confirmed that imidazolium ring didn't come into the β -CD cavity.¹⁶ What's more, they also found that vesicle was formed in the system and the vesicle will become lamellae hydrogel if lower the temperature, which is reversible and reproducible.¹⁷ In short, ILs and CDs can form inclusion complexes by host-guest interactions. However, all of these are about the formation and mechanism of ILs and CDs inclusion complexes, or the changes of physicochemical properties of ILs system by adding cyclodextrins. Self-assembly of adamantane-based ionic liquid by adding CDs at different molar ratios were seldom discussed.

Adamantane is a symmetric tricyclic hydrocarbon composed of 10 carbon atoms and 16 hydrogen atoms,^{18–20} and it was a classic guest molecular for β -CD owing to its high association constants. In this work, a cationic adamantane-based ionic liquid, AD- C_{11} im (the chemical structure shown in Fig. 1), has been synthesized from 1-adamantanecarboxylic acid. The synthesis route is illustrated in the ESI (Scheme S1[†]). Thus, the AD- C_{11} im molecular can provide two binding sites for β -CD: one is alkane chain; the other is adamantane.^{21,22} Different binding sites may lead to form different building blocks due to host-guest interaction, and then form diverse aggregate morphology. Hence, it will be very interesting to investigate the binding sites of AD- C_{11} im and the aggregate morphology transformation by adding β -CD at different molar ratios. For better understanding the effects on the aggregate morphology of AD- C_{11} im by adding β -CD the host-guest inclusion compounds formed by AD- C_{11} im and β -CD at diverse molar ratios were discussed.

Experimental

Materials and apparatus

The synthetic process and treatment of 11-bromoundecyl adamantane-1-carboxylate are mentioned in our previous article.²⁰ 11-Bromo-1-undecanol, *p*-toluenesulfonic acid monohydrate, 1-methylimidazole, β -cyclodextrin were acquired from Energy Chemical and used as received. Reagent grade materials were prepared. High-purity water (18.25 M Ω cm) was used to prepare all aqueous solutions.

¹H NMR, ¹³C NMR and ¹H-¹H 2D ROESY NMR measurements were performed on Bruker Avance-400 spectrometer operating at 400 MHz. ESI-MS was carried out on a mass

spectrometer (6120 Single Quad, Agilent). Electrical conductivity of samples was performed on conductivity meter at 25 °C (DDS-307A, Rex Shanghai). Moisture should be removed prior to FT-IR measurements (Spectrum Two, PerkinElmer).

Samples preparation

The samples were prepared *via* mixing AD- C_{11} im and β -CD in proportion with 1 : 1 or 1 : 2 in aqueous solution and heated to get hyaline solutions in succession. After that, the mixtures were kept at room temperature for one day at any rate to form aggregates. The summation of AD- C_{11} im was used as the molar concentration of inclusion in the mixture system in the article and the AD- C_{11} im concentration changed from 5 to 100 mM.

Thermogravimetric (TG) tests

Thermogravimetric (TG) tests were performed on a TGA 4000 PerkinElmer instrument, each sample was heated at a rate of 10 °C min⁻¹ from 50 °C to 500 °C under N₂ atmosphere. The inclusion complexes of AD- C_{11} im and β -CD were prepared by suspension method and then dried. The physical mixtures were obtained by mixing the pure of AD- C_{11} im and β -CD.²³

Dynamic light scattering (DLS)

The hydrodynamic sizes of samples were determined by Zetasizer (Malvern, UK). All samples were conducted at room temperature with 633 nm laser light and the scattering angle was fixed at 90°. Before examination, the samples were filtered through a 450 nm filter.

Transmission electron microscopy (TEM)

The morphology of these samples was studied using transmission electron microscope working at 200 kV (FEI, USA). A spot of the sample was put onto a copper mesh coated with carbon, and then prepared with negative-staining. The superfluous solution was wiped away with filter paper cautiously, and the samples were then air-dried for TEM observation.

Atomic force microscopy (AFM)

AFM images were obtained using Icon scanning probe microscope (Bruker, USA). A 5 μ L portion of the sample was put onto caller mica. Two minutes later, the excess aqueous solution was wiped away with filter paper carefully, and the sample-loaded mica was air-dried for AFM observation in Tapping Mode.

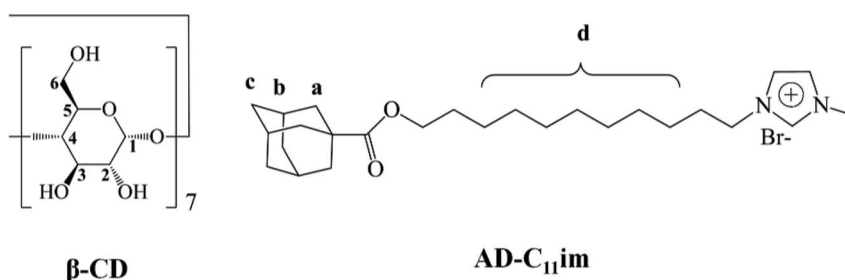


Fig. 1 Molecular structures of β -CD and AD- C_{11} im.



and H-5 are hydrons that located in the lumen of β -CD. When the guest molecule enters the cavity, the shielding effect will cause the proton chemical shifts of them.^{26,27} Thus, Job's curves,^{19,28} same to our previous research methods,²⁰ were plotted by measuring the chemical shifts of H-3 and H-5 at different concentration ratios to check the maximum stoichiometry of AD-C₁₁im/ β -CD system, which were shown in Fig. 3. From Fig. 3, when $r = 0.67$, the Job's curves of both H-3 and H-5 obtained the peak, which meant that the molar ratio of AD-C₁₁im/ β -CD system was 1 : 2, that is to say, one AD-C₁₁im can combine with not more than two cyclodextrins.

It has been proved that the maximum stoichiometry of AD-C₁₁im/ β -CD system was 1 : 2. According to the literature data, the adamantane can combine with β -CD and the binding constant is 10^5 M^{-1} ,^{26,29,30} which is stronger than that of alkyl chain (almost 10^3 M^{-1}) in aqueous solution.^{22,31,32} Thus, it will be very interesting to explore the inclusion site of β -CD at different molar ratios.

As is known to all, hydrophobic chain is quite important for foaming capacity of surfactants. Hence, foaming ability and foam stability can indirectly reflect whether the hydrophobic chain is encapsulated by β -CD.³³ Once the alkyl chain enters into the β -CD cavity, the foam formed by surfactant would be destroyed. In order to confirm this, a control test of foamability in different system was launched. Photos in Fig. 4 reflected that a lot of foams were appeared when the system was AD-C₁₁im itself or a 1 : 1 system, indicating the alkyl chain was not encapsulated by β -CD when the molar ratio was 1 : 1. At the same time, the foam vanished quickly when the molar ratio was 1 : 2. It states the hydrophobic chain was encapsulated by β -CD. Furthermore, to confirm the formation of AD-C₁₁im@2 β -CD inclusion complexes, the thermogravimetric (TG) tests were performed. Results were exhibited in Fig. S4.† As shown in Fig. S4,† the TG patterned illustrated that pure AD-C₁₁im and β -CD decomposed at about 85 and 301 °C, separately. Compared the TG curve of AD-C₁₁im/ β -CD inclusion complexes with physical mixtures, it is not difficult to find that the inclusion complexes possessed high decomposition temperature, which implies that the AD-C₁₁im@2 β -CD host-guest inclusion complexes were indeed formed.

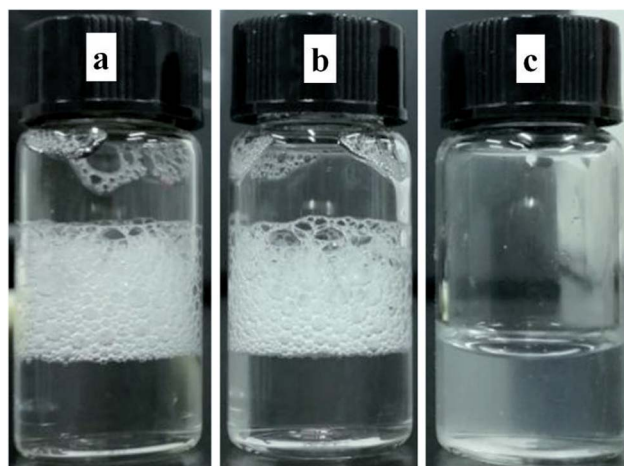


Fig. 4 Foam generated by 10 mM AD-C₁₁im (a), 10 mM AD-C₁₁im@1 β -CD (b), and 10 mM AD-C₁₁im@2 β -CD (c).

¹H-¹H 2D ROESY NMR, which can reflect the interaction between hydrogen atoms with space distance less than 0.5 nm, is an effective way to study host-guest inclusion interaction. In order to confirm the formation of inclusion complexes between AD-C₁₁im and β -CD at different molar ratios, 2D ROESY spectra of AD-C₁₁im/ β -CD inclusions in proportion of 1 : 1 and 1 : 2 were performed and data were exhibited in Fig. 5. As shown in Fig. 5a, correlation signals of H-3 and H-5 in β -CD molecular with methylene and tertiary hydrogen in adamantane were detected (marked by squares). Nevertheless, the correlations between H-3 and H-5 and alkyl chain were not found. Simultaneously, Fig. 5b revealed that correlation signals of H-3 and H-5 with adamantane group (marked by squares) and alkyl chain (marked by circles) were both tested. Based on these data, it can be concluded that just adamantane group was encapsulated by β -CD and the alkyl chain in the molecule was not encapsulated in a 1 : 1 system, thus forming the inclusion compound AD-C₁₁im@1 β -CD. Furthermore, both adamantane group and alkyl chain were encapsulated by β -CD in a 1 : 2 system, forming the inclusion compound AD-C₁₁im@2 β -CD.

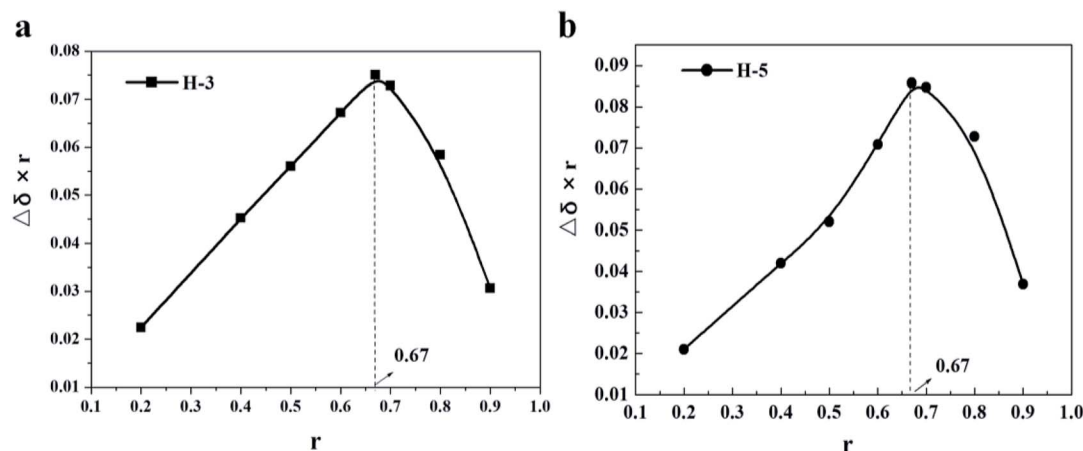


Fig. 3 ¹H NMR Job's curves base on H-3 (a), and H-5 (b) of β -CD in D₂O.



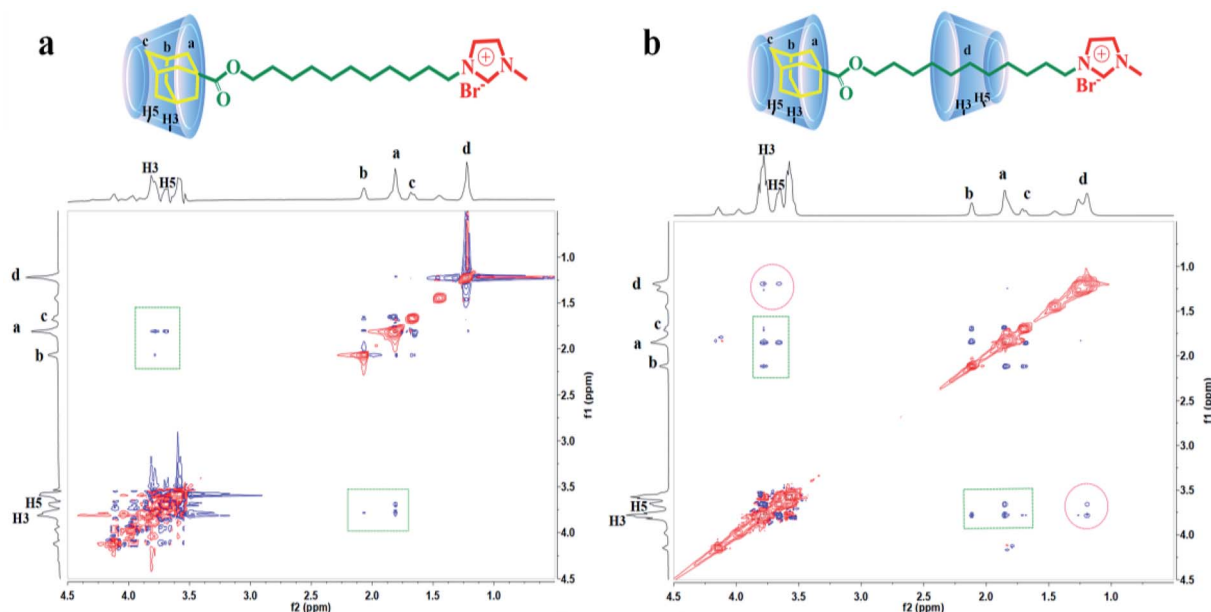


Fig. 5 ^1H - ^1H 2D ROESY spectra of 10 mM AD-C₁₁im@1β-CD (a) and 10 mM AD-C₁₁im@2β-CD (b).

Self-assembling behaviors of AD-C₁₁im@1β-CD

Inclusion compound AD-C₁₁im@1β-CD, which was obtained by adding β-CD into AD-C₁₁im aqueous solution at a molar ratio of 1 : 1, can be regarded as an asymmetric bola amphiphilic molecule with imidazole and β-CD as the head group. To investigate micelle aggregates formed by AD-C₁₁im when adding the same amount β-CD, DLS were employed for AD-C₁₁im@1β-CD at 10 mM (shown in Fig. 6a by scattering intensity and Fig. S5† by volume). Compared with the DLS results for AD-C₁₁im, the average hydrodynamic radius (Rh) values of 10 mM AD-C₁₁im@1β-CD inclusion were about 186 nm and 164 nm by scattering intensity and volume, respectively. The AD-C₁₁im@1β-CD inclusion was much larger than AD-C₁₁im at the same concentration. This suggested the formation of new aggregation different from the micelles formed by AD-C₁₁im itself. To make clear the morphology of the new aggregation, the negative-staining TEM of AD-C₁₁im@1β-CD at 10 mM was tested and pictures were exhibited in Fig. 6b and c. The result of TEM illustrated that spherical vesicles (marked with pink arrows in Fig. 6b), the diameter of which varied from 60 to 110 nm, formed after adding β-CD into AD-C₁₁im aqueous solution at a molar ratio of 1 : 1. The diameter of TEM was smaller than that of DLS and it may be the result of drying process before TEM measurement. What's more, the polygonal aggregates proved to be formed by β-CD were observed in Fig. 6b (marked with yellow dashed arrow).¹⁹

In order to confirm the arrangement of AD-C₁₁im@1β-CD in the vesicle structure, AFM was measured and results were shown in Fig. 7. Vesicle structure, similar to TEM, was found from AFM results shown in Fig. 7a and diameters of these spherical aggregates arranged from 60 nm to 110 nm, which was same with TEM results. Two spherical aggregates were selected to investigate the thickness of vesicle wall and the heights (shown in Fig. 7b) were 5.88 nm and 5.41 nm, separately. It can be concluded that the average wall thickness of

these vesicles was around 2.82 nm basically equivalent to the size of AD-C₁₁im@1β-CD (2.85 nm) calculated according to Corey–Pauling–Koltun (CPK) model shown in Fig. 7c. Therefore, the conclusion that AD-C₁₁im@1β-CD molecules are arranged in a single layer in the vesicle wall rather than in a double layer can be drawn from the results described above.¹⁹

As an asymmetric bola amphiphilic molecule with two head group, one of them has positive charge (the imidazole ring) and the other has no charge (β-CD). Thus, the zeta potential (ζ) measurement may be useful to make a thorough inquiry about how the AD-C₁₁im@1β-CD molecules arrayed in the vesicle wall.^{34,35} Due to AD-C₁₁im containing an imidazole group with positive charge, the zeta potential value of micelles formed by AD-C₁₁im only was +32.3 mV in aqueous solution when the concentration was 10 mM. However, the ζ value of vesicles formed by AD-C₁₁im@1β-CD at 10 mM was just +10.4 mV, which was much smaller than that of AD-C₁₁im. It means that a majority of these asymmetric bola amphiphilic molecules existed in the arrangement of the non-charged large-head cyclodextrin group in the outer wall and the charged pyridine group in the inner wall and formed single-layer vesicle, which was asymmetrical in the inner and outer surfaces.

Self-assembling behavior of AD-C₁₁im @2β-CD

β-CD was added to the vesicle formed by AD-C₁₁im@1β-CD until the molar ratio of AD-C₁₁im: CD was 1 : 2 and superfluous β-CD would be combined with the alkyl chain. In the light of the literature and the above findings, it can be considered that the great majority of alkyl chains in AD-C₁₁im molecular were embodied in the cavity of β-CD, which was treated as AD-C₁₁im@2β-CD. With the increasing of AD-C₁₁im@2β-CD concentration, the appearance of the sample changed a lot, which was discussed in Phase diagrams of AD-C₁₁im/β-CD





Fig. 6 DLS (a) and TEM ((b) scale bar = 200 nm, (c) scale bar = 100 nm) results of 10 mM AD-C₁₁im@1 β -CD.

system section. Consequently, the information on morphologies of these aggregates will be discussed in detail below.

To identify the morphology, transmission electron microstructure were observed in AD-C₁₁im@2 β -CD system, shown in Fig. 8. The TEM observation results indicated that fibers, which were similar to Zukoski's studies,³⁶ emerged in AD-C₁₁im@2 β -CD system when the concentration of AD-C₁₁im@2 β -CD was 30 mM. The diameters of the fibers varied from 20 nm to 40 nm shown in Fig. 8a. Considering that the diameters of fibers were in nano-scale, the morphology of aggregates in AD-C₁₁im@2 β -

CD system can be reported as nanofibers. Besides, these nanofibers were found to intertwine with each other shown in Fig. 8b and hence these nanofibers can be considered to be net-like nanofibers, which may be responsible for the non-transparent and viscoelastic appearance in Fig. 2d. The Small Angle X-Ray Scattering (SAXS) for AD-C₁₁im@2 β -CD at 30 mM to receive the nanostructures morphology. As shown in Fig. S7,[†] It can be seen that there is no obvious Bragg diffraction peak in the SAXS spectrum. SAXS test implied that the structure of net-like nanofibers was disordered.



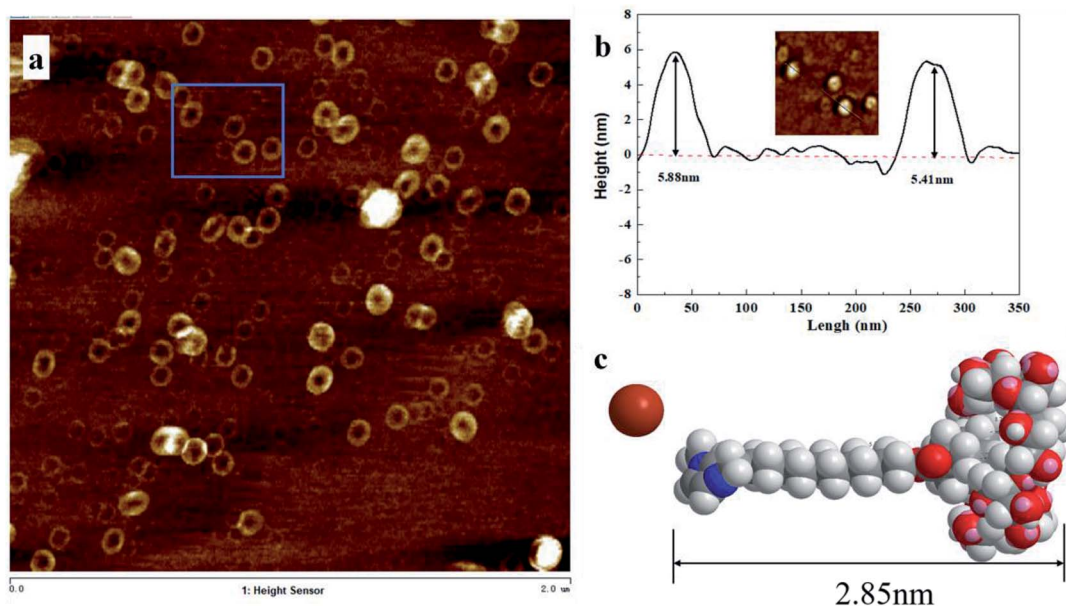


Fig. 7 (a) AFM image for aggregates from 10 mM AD-C₁₁im@1β-CD. (b) Sectional height profile of collapsed vesicles. (c) Molecular structure model of inclusion complex AD-C₁₁im@1β-CD.

With the increase of AD-C₁₁im concentration (above 35 mM), the solution did not flow even by inversion of the vial, indicating the formation of hydrogel. It is considered that gelation occurred because of cross-linked fibrillar networks. SEM is one of the most effective methods to study the morphology of hydrogel.^{37,38} The SEM observation results in Fig. 9 showed that honeycomb structure caused by evaporation of water was appeared in the hydrogel, which meant the three-dimensional (3D) interconnected networks microstructure shaped.

FT-IR analysis of AD-C₁₁im@nβ-CD

It is generally known that hydrophobic interaction is mainly caused by alkyl chain. Hydrophobic interaction will not work

during formation process of aggregates if alkyl chain is included in β-CD. According to ¹H-¹H 2D ROESY NMR of AD-C₁₁im@nβ-CD inclusions, the alkyl chain in the molecule was not encapsulated in a 1 : 1 system, but encapsulated in a 1 : 2 system. The results indicated that there were hydrophobic regions when the aggregates formed in AD-C₁₁im@1β-CD system and it was believed that there was almost no hydrophobic region when the aggregates shaped in AD-C₁₁im@2β-CD system. Accordingly, hydrophobic interaction was no longer the major driving force during forming process of aggregates in AD-C₁₁im@2β-CD system.

Compared with AD-C₁₁im itself, the hydrophobicity of AD-C₁₁im@nβ-CD inclusions decreased greatly owing to abundant

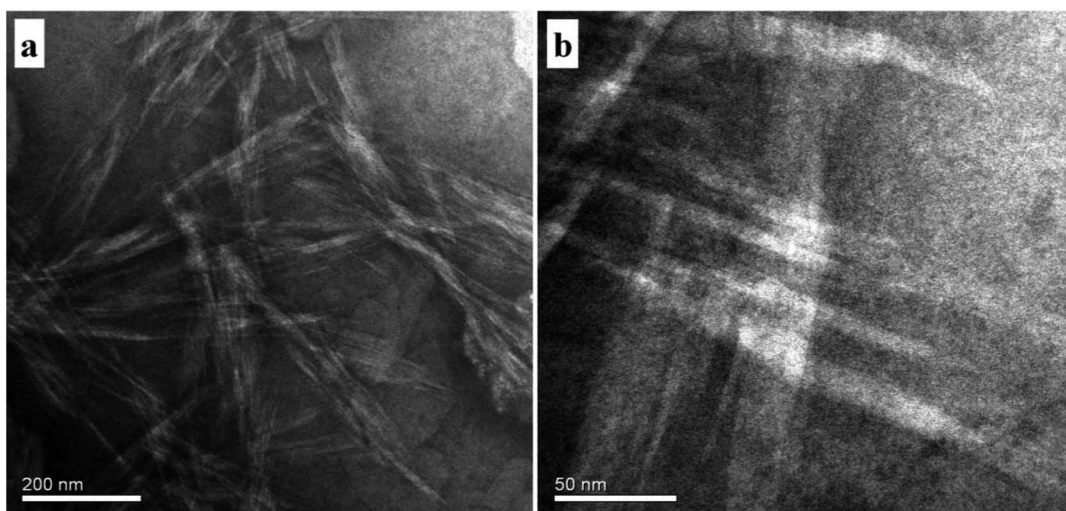


Fig. 8 TEM images of 30 mM AD-C₁₁im@2β-CD. (a) Scale bar = 200 nm. (b) Scale bar = 50 nm.



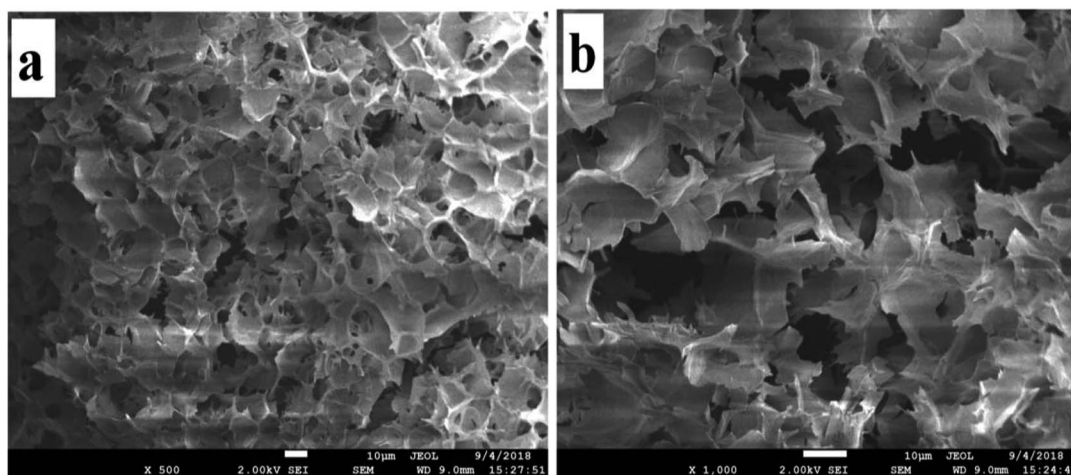


Fig. 9 SEM images of the hydrogel system with 50 mM AD-C₁₁im@2β-CD.

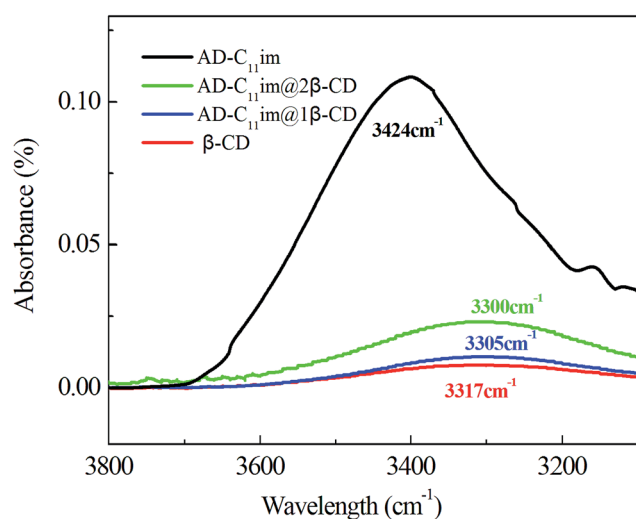


Fig. 10 FT-IR spectra for β-CD, AD-C₁₁im, AD-C₁₁im@1β-CD, AD-C₁₁im@2β-CD.

hydroxyl on the outer surface of β-CD. Thus, hydrogen bonding may play a key role. For this reason, the FT-IR spectra of β-CD, AD-C₁₁im@1β-CD and AD-C₁₁im@2β-CD samples were investigated and results were exhibited in Fig. 10 and Fig. S6.† It is

easy to see that the hydroxyl stretching vibration peak of pure CD was located at 3317 cm⁻¹. However, these of AD-C₁₁im@1β-CD and AD-C₁₁im@2β-CD samples were located at 3305 cm⁻¹ and 3300 cm⁻¹ separately. Both of them moved to the low wavenumber region. This revealed that a stronger hydrogen bond interaction was formed between β-CD during formation process of aggregates.³⁹

In a word, it can be deduced that the self-assembly process should be driven mainly by hydrogen bonds between β-CD in AD-C₁₁im@2β-CD system. To prove this conclusion, a representative gel sample (AD-C₁₁im@2β-CD at 50 mM) was selected. From Fig. 11, it can be seen that the bluish hydrogel (Fig. 11a) started to flow when it was heated to 45 °C and then turned into transparent solution (Fig. 11c) when temperature was more than 80 °C. However, the gel was formed again after cooling. This indicates that hydrogen bonds between β-CD play a key role in AD-C₁₁im@2β-CD system.

Based on the above experimental data, AD-C₁₁im micelles transformed into other aggregate morphologies by adding β-CD are described in detail in Scheme 1. AD-C₁₁im, like traditional single chain surfactants, can be self-assembled into micelles in dilute aqueous solutions with hydrophilic imidazoles on the outer surface of micelles and hydrophobic adamantane in the core. However, the asymmetric bola-type amphiphilic molecule

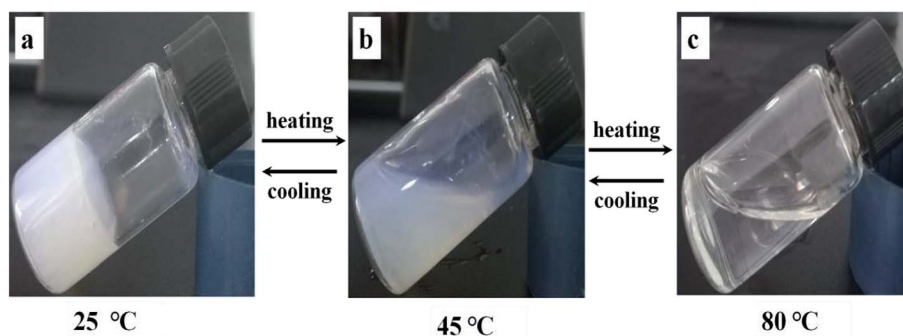
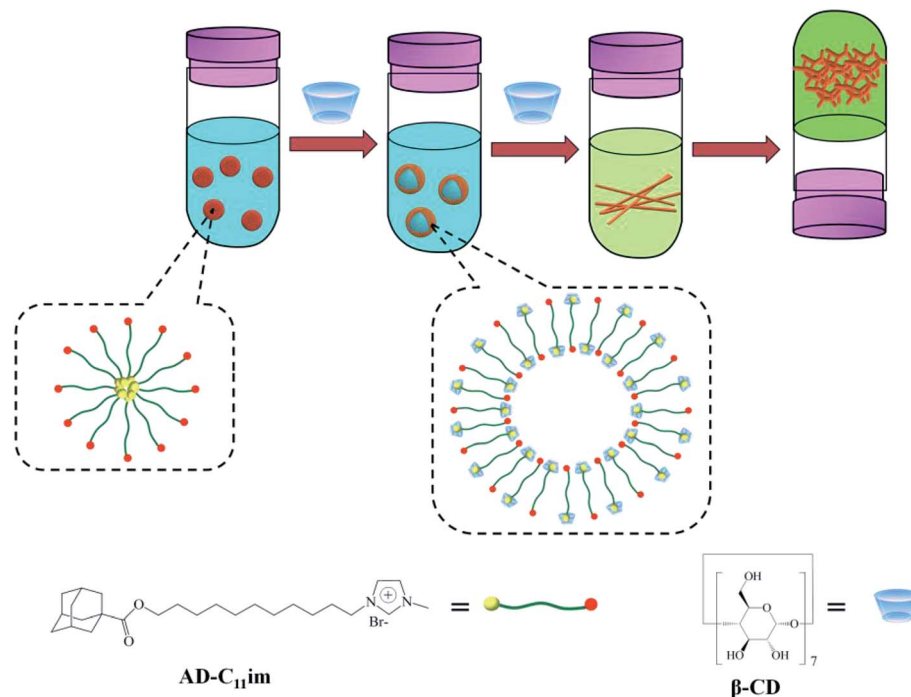


Fig. 11 Gel-sol transformation process of 50 mM AD-C₁₁im @2β-CD. (a) Hydrogel at 25 °C, (b) mesophase at about 45 °C, (c) clear solution at about 80 °C.





Scheme 1 Schematic diagram of the aggregation transformation of AD-C₁₁im induced by β -CD.

(AD-C₁₁im@1 β -CD) was formed by the host-guest interaction between adamantane and β -CD after adding same molar amount of β -CD. Thus, hydrophobicity between alkane chains and hydrogen bonding between β -CD were the main driving forces, and asymmetric vesicles with the uncharged cyclodextrins in the outer wall and the charged pyridine group in the inner wall formed. When adding a double molar amount of β -CD, both adamantane and alkyl chain in AD-C₁₁im molecule were encapsulated by β -CD and the hydrophobic interaction was destroyed, which was no longer the main driving force. Then the building blocks (AD-C₁₁im@2 β -CD inclusion) became unamphiphilic and driven by hydrogen bonding between β -CD to form net-like nanofiber. With the increase of AD-C₁₁im@2 β -CD concentration, hydrogen bonding between β -CD strengthened and net-like nanofibers started to overlap and interweave. During the process, water molecules padded the spaces during the nanofibers.⁴⁰ As a result, the hydrogel with three-dimensional (3D) interconnected networks microstructure appeared.

Conclusions

All in all, a novel synthesized adamantane-based ionic liquid, AD-C₁₁im, was proved to have surface activities and can form micelles by electrical conductivity and DLS. What's more, the aggregation transformation of AD-C₁₁im by adding β -CD in different molars was investigated. Results showed that when the same amount β -CD was added in AD-C₁₁im aqueous solution, just adamantane was encapsulated by β -CD and the asymmetric bola-type amphiphilic molecule (AD-C₁₁im@1 β -CD) was formed by the host-guest inclusion reaction between adamantane and β -CD. As a result, micelles were translated to vesicles, which were confirmed by DLS and TEM. Moreover, the vesicles were

proved to be single-layer structure by AFM. When adding a double molar amount of β -CD, ¹H-¹H 2D ROESY NMR results revealed that apart from adamantane, alkyl chain was also wrapped by β -CD. Driven by hydrogen bonding between β -CD, net-like nanofibers were found by TEM. With an increase in the AD-C₁₁im@2 β -CD concentration up to 40 mM, net-like nanofibers became denser, started to intertwine with each other, and then the bluish hydrogel formed.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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