Soft Matter

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

# A case of cyclodextrin-catalyzed self-assembly of an amphiphile into microspheres†

Cite this: *Soft Matter*, 2013, **9**, 7710

Li Zhao,[a] Lingxiang Jiang,[a] Yuchun Han,[b] Zhaoyang Xian,[a] Jianbin Huang*[a] and Yun Yan*[a]

Received 3rd May 2013
Accepted 6th June 2013

DOI: 10.1039/c3sm51235e

**www.rsc.org/softmatter**

One of the recent challenges in nanotechnology is the development of 'catalyzed self-assembly'. So far successful cases are still scarce. In this work we report the delicate case of a cyclodextrin (CD) catalyzed self-assembly of the terthiophene-containing amphiphile TTC4L into microspheres. TT4CL can form precipitates when CDs are not present, whereas it self-assembles into microspheres in the presence of CDs. The CDs were not involved into the microspheres, but they stayed in the supernate in the form of the TTC4L@CD inclusion complex. This complex may further transform into microspheres in the presence of a competitive guest. ITC and $^1$H NMR measurements suggest that part of the terthiophene group binds weakly with CDs. We expect that this weak binding interferes with the quick stacking of TTC4L, so that a 'slow' arrangement of the terthiophene moiety becomes possible which finally leads to the formation of microspheres. Our results not only provide a new solid example of a catalyzed molecular self-assembly, but also envisage a new paradigm for the possible role of CDs in supramolecular chemistry.

## Introduction

Various molecular self-assemblies have attracted immense attention in chemistry,[1–3] materials science,[4–6] and biology[7–9] owing to the important roles that they play in these fields. The driving forces for the self-assembling process often include hydrophobic interactions,[10] hydrogen bonding,[11] π–π stacking,[12] coordinating,[13] and electrostatic interactions.[14] The self-assembly of discrete molecules into certain organized structures is often spontaneous since the assembly of the molecules may bring the system to a lower energy state. However, many molecules do not easily self-assemble; certain assistance, such as an external energy input, or a proper initiating component, has to be offered to obtain the desired structures. For example, many self-assemblies are formed upon exposure to an electro-field,[15] X-rays,[16] infrared light,[17] a magnetic field,[18] ultrasound,[19] *etc.*

There are also self-assemblies that are realized in the presence of another component, such as the self-assembly of unlike homopolymers into hollow spheres in a nonselective solvent,[20] and the switching of supramolecular polymeric materials with different length scales.[21] A similar case to ours was observed based on the self-assembly of cucurbit[*n*]uril. An amphiphile is required to form host–guest inclusion complexes before the self-assembly of cucurbit[*n*]uril, in this example the amphiphile is released when nano crystals of cucurbit[*n*]uril are formed.[22] In analogy, protons were found to assist the self-assembly of linear dipyridyl polyaromatic molecules at a solid–liquid interface.[23] Such assisted self-assembly also occurs in biological systems. For instance, the dimerization of chloroeremomycin (CE) can be enhanced in the presence of indole-carboxylic acid. Further study demonstrated that the indole-carboxylic acid (ICA) shortened the distance between the two CE molecules by the formation of multiple hydrogen bonds with them. ICA then leaves since the hydrogen bonding between the CE molecules is stronger than it is between CE and ICA.[24] These studies suggest that some molecular self-assemblies can be 'catalyzed' by an inducing component which does not appear in the final self-assembled structures. From this point of view, they can be viewed as 'catalysis' for the self-assembly process. It has been anticipated that 'catalyzed self-assembly' may be used to construct state-of-the-art materials in this decade.[25,26] However, successful cases of catalyzed self-assembly are still scarce.

Herein we report a case of CD catalyzed molecular self-assembly. Cyclodextrins (CDs) are the most frequently used hosts for a large variety of guests owing to the presence of their hydrophobic cavities.[27–32] CD inclusion complexes are often hydrophilic owing to the presence of multiple OH groups on the outer surface of the CDs.[33–36] As a result, amphiphiles usually lose their ability to aggregate or self-assemble upon inclusion

---

[a] *Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, P. R. China. E-mail: yunyan@pku.edu.cn; jbhuang@pku.edu.cn*

[b] *Institute of Chemistry, Chinese Academy of Sciences, Beijing, China*

† Electronic supplementary information (ESI) available: Species distributions and turbidity curve of TTC4L; SEM images of precipitate formed in TTC4L and TTC4L@β-CD systems. See DOI: 10.1039/c3sm51235e

with CDs in aqueous media.[29,37–39] Very recently, our group found that the hydrophilic inclusion complexes may further self-assemble into vesicles, multi-walled tubes, and lamellae *via* hydrogen bonding at high concentrations.[29,30,33,40–42] These novel CD–guest self-assemblies frequently happened suggesting that the role of CDs in molecular self-assemblies is far from understood, which inspired us to explore other possible uses of CDs in building self-assembled molecular structures.

In this work we report that CDs 'catalyze' the self-assembly of the terthiophene-containing amphiphile TTC4L (Scheme 1) in to microspheres. Without the assistance of CDs, TT4CL may form irregular precipitates upon acidification, whereas they self-assemble into microspheres in the presence of CDs. The CDs were not involved in the microspheres, suggesting that they acted in a 'catalytic' manner in the self-assembly process. Our results not only provide a new solid example of a catalyzed molecular self-assembly, but also envisage a new paradigm for the possible role of CDs in supramolecular chemistry.

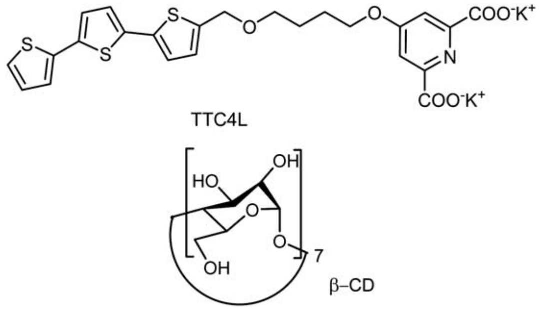
## Experimental

### Material

TTC4L was synthesized according to the procedure reported in our previous work.[43] β-Cyclodextrin (β-CD) was purchased from Sinopharm Chemical Reagent Co. with a water content of 13% and was used without further treatment. 1-Adamantanamine hydrochloride (AdaHC, 99%, J&K Scientific Ltd.) was used after purchase without further purification. α-Amylase from *Aspergillus oryzae* (Sigma, ~30 units per mg) was used as received.

### Sample preparation

The solutions were obtained by dissolving the solid TTC4L powder in ultrapure water (Milli-Q, 18.2 MΩ cm). The pH of the TTC4L solutions was adjusted to about 12 by adding tiny amounts of concentrated KOH aqueous solution (about 1 M). The TTC4L@β-CD solutions were prepared by dissolving TTC4L and β-CD powder of a corresponding weight in ultrapure water. The concentration of TTC4L was kept at 0.5 mM for all measurements. These samples were vortex mixed and kept at 25 °C. Then concentrated aqueous solution of HCl (about 1.3 mM) was added slowly to the TTC4L@β-CD solutions to get precipitates. 1 μL HCl solution was added in each addition. Then the solution was allowed stand still to reach equilibrium. The pH at equilibrium was recorded after each addition using a SevenMulti type pH meter with InLab Semi-Micro electrodes (Mettler Toledo, Switzerland). All analytical measurements were performed at 25 °C.



**Scheme 1** Molecular structures of TTC4L and β-CD.

### Characterization

**Spectra measurements.** A Hitachi F-4500 fluorescence spectrometer was used to measure the fluorescence emission of the microspheres. The excitation wavelength was set at 360 nm. Emission spectra were recorded in the range of 375–700 nm. UV spectra for all the samples were collected on a Pgeneral TU-1810 UV-vis spectrophotometer. The microscopic Fourier transform IR spectra were collected with a Nicolet iN10 MX spectrometer (Thermo Scientific, America) operating in the range of 4000 to 600 $cm^{-1}$. The $^1H$ NMR experiments were performed on a Bruker-500 ($^1H$: 500 MHz) spectrometer with $D_2O$ as the solvent at 25.0 °C.

**XRD measurements.** Several drops of the suspension were dropped on a clean glass slide followed by drying in air. Reflection XRD studies were carried out on the film with a model XKS-2000 X-ray diffractometer (Scintaginc). The X-ray beam was generated with a Cu anode, and the wavelength of the $K_{\alpha1}$ beam was 1.5406 Å. The X-ray beam was directed toward the film edge, and the scanning was done in the $2\theta$ range from 0.6–8° and 3–40°.

**SEM measurements.** Field-emission scanning electron microscopy (FE-SEM) images were taken with a Hitachi S4800. For the SEM measurements, the obtained products were washed with water several times, and then were dispersed in water and dropped onto a silicon wafer, followed by drying naturally.

**Isothermal titration microcalorimetry.** All measurements were performed in a TAM 2277-201 microcalorimetric system (Thermometric AB, Järfälla, Sweden) with a stainless steel sample cell of 1 mL. The sample cell was initially loaded with 0.7 mL of solvent or surfactant solution. The β-CD solution was injected into the sample cell *via* a 500 μL Hamilton syringe controlled by a 612 Thermometric Lund pump. A series of injections were made until the desired concentration range had been covered. The system was stirred at 60 rpm with a gold propeller. The observed enthalpy ($\Delta H_{obs}$) was obtained by integration over the peak for each injection in the plot of heat flow $P$ against time $t$. The dilution heats of the β-CD solution were subtracted from the heats of the binding experiments. The data fitting was performed by using the computer program for TAM (Digitam 4.1 for Windows from Thermometric AB). By fitting the observed enthalpy curves plotted against the molar ratio of β-CD to surfactant, the binding stoichiometry $n$, binding constant ($K$) and the binding enthalpy ($\Delta H$) were derived. All of the measurements were conducted at 298.15 ± 0.01 K.

## Results and discussion

The amphiphile TTC4L used in this study was developed in our lab (Scheme 1).[43] Two p$K_a$s, namely, $pK_{a1} = 4.6$ and $pK_{a2} = 7.9$, can be obtained according to the pH titration experiments

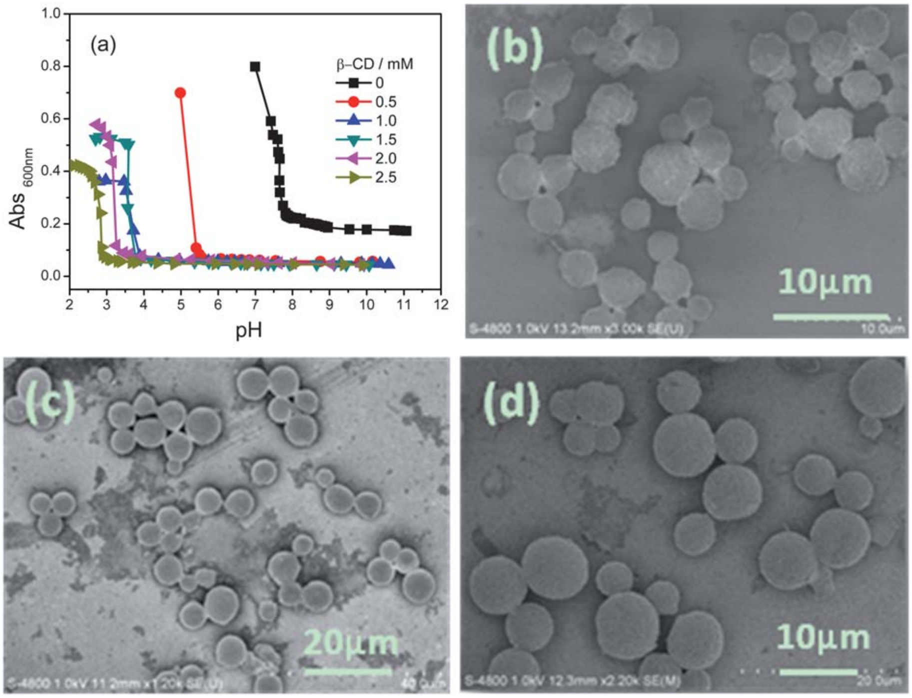


**Fig. 1** (a) Turbidity curves of TTC4L@β-CD complex systems at various concentrations of β-CD. (b–d) SEM images of the precipitates formed in the TTC4L@β-CD systems at various TTC4L to β-CD molar ratios. The concentration of TTC4L in all samples is fixed at 0.5 mM, while [β-CD] = 0.5 mM, 1.5 mM, and 2.5 mM, respectively, from (b) to (d). The precipitates were obtained when pH was lower than their critical precipitation pH as demonstrated in (a).

**Table 1** Elemental analysis results for the precipitates obtained in different conditions. For comparison, the calculated results for TTC4L molecules in $H_2A$ ($C_{24}H_{21}NO_6S_3$) and $HA^-$ ($C_{24}H_{20}KNO_6S_3$) forms and that of β-CD are also listed

| [β-CD]/[TTC4L] | C% (wt%) | N% (wt%) | H% (wt%) | C/N (molar ratio) |
|---|---|---|---|---|
| 0 | 52.97 | 2.41 | 3.95 | 25.66 |
| 1 | 53.32 | 2.42 | 4.05 | 25.60 |
| 3 | 53.30 | 2.38 | 4.14 | 26.15 |
| 5 | 52.88 | 2.38 | 3.97 | 25.90 |
| $C_{24}H_{20}KNO_6S_3$ calcd | 52.31 | 2.55 | 3.67 | 24.0 |
| $C_{24}H_{21}NO_6S_3$ calcd | 55.90 | 2.72 | 4.11 | 24.0 |
| β-CD ($C_{42}H_{70}O_{35}$) | 44.45 | | 6.22 | |

(Fig. S1†). If we consider the TTC4L molecule in the form of $A^{2-}$, it can be expected that $A^{2-}$ will become dominant only at pH > 7.9. $HA^-$ may occur when pH is between 4.6 and 7.9. This resulted in TTC4L having poor solubility in pure water, so that solely pale yellow dispersions were obtained at concentrations below 1 mM, whereas precipitates occurred at higher concentrations. In Fig. 1a the turbidity curve with black squares indicates that TTC4L forms a clear solution at pH > 8.0, in line with the pH titration results; whereas it precipitates drastically at pH below 7.0, suggesting that TTC4L in the form of $HA^-$ exhibits poor solubility. However, in the presence of β-CD, the solubility can be greatly enhanced and precipitation occurs at a much lower pH. It is very striking in Fig. 1a that the critical pH where precipitation occurs can be lowered to pH 2.9 with an increased fraction of β-CD. No further change in the precipitation pH can be observed for the 0.5 mM TTC4L system as [β-CD] exceeds 2.5 mM. TEM observations revealed that the precipitates obtained at pH 7.0, when no β-CD was added to the system, are irregular (Fig. S2†), whereas microspheres were observed for all of the precipitates in the β-CD participated systems (Fig. 1b–d and Fig. S3†). It is found that the critical [β-CD] for the formation of microspheres in the 0.5 mM TTC4L system is 0.5 mM. Lower [β-CD] cannot effectively lead to microsphere formation.

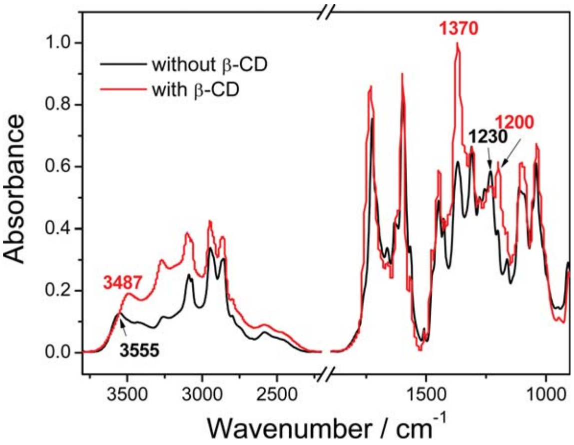


**Fig. 2** IR spectra for the precipitates of TTC4L obtained with and without β-CD.

Elemental analysis reveals that the C/N ratios for the microspheres obtained at various pH are all around 25.60–26.15, which is very close to the expected value of 24 for the TTC4L molecule (Table 1). Since the proportion of C in these microspheres is around 53%, which is close to the calculated C

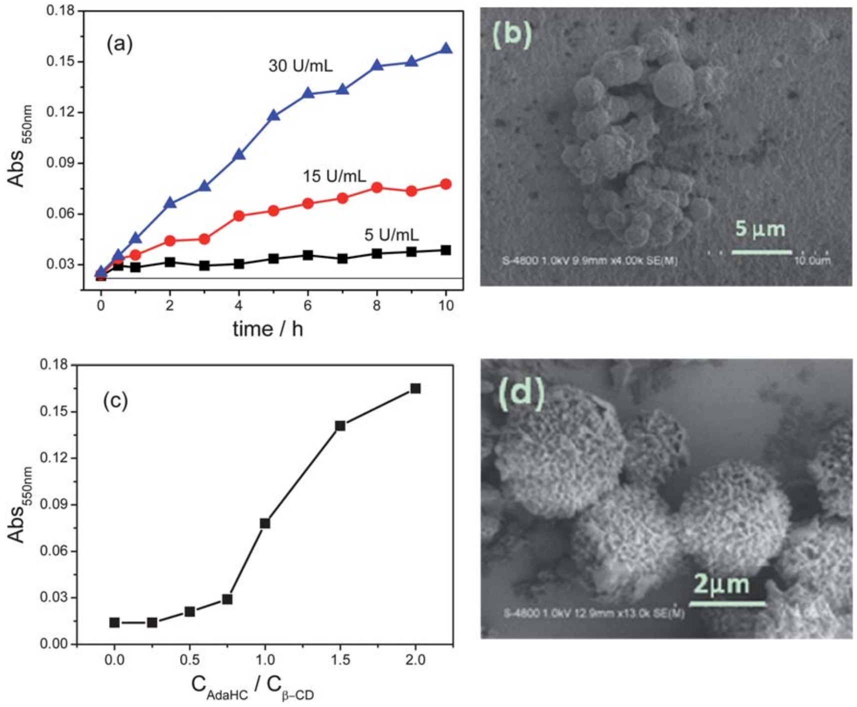


**Fig. 3** Turbidity curves of the TTC4L@β-CD solution at pH ~ 3–4 upon addition of (a) α-amylase or (c) AdaHC. SEM images of the precipitates, (b) that resulted from (a), and (d) that resulted from (c).

content in TTC4L (52.3–55.9, depending on the acidification degree, Table 1) but is considerably higher than that in β-CD (44.45%), the presence of β-CD in the microspheres can be ruled out.

In Fig. 2 we show the IR spectra for the precipitates obtained with and without β-CD, respectively. A slight difference can be discerned for the vibration of the hydrogen bonds and that of the COO groups. The hydrogen bond stretching vibration can be recognized at 3555 $cm^{-1}$ for the irregular precipitates, whereas it moves down to 3487 $cm^{-1}$ for the microspheres, suggesting that the hydrogen bonding becomes stronger as the pH decreases when β-CD was added. In line with this, the vibration

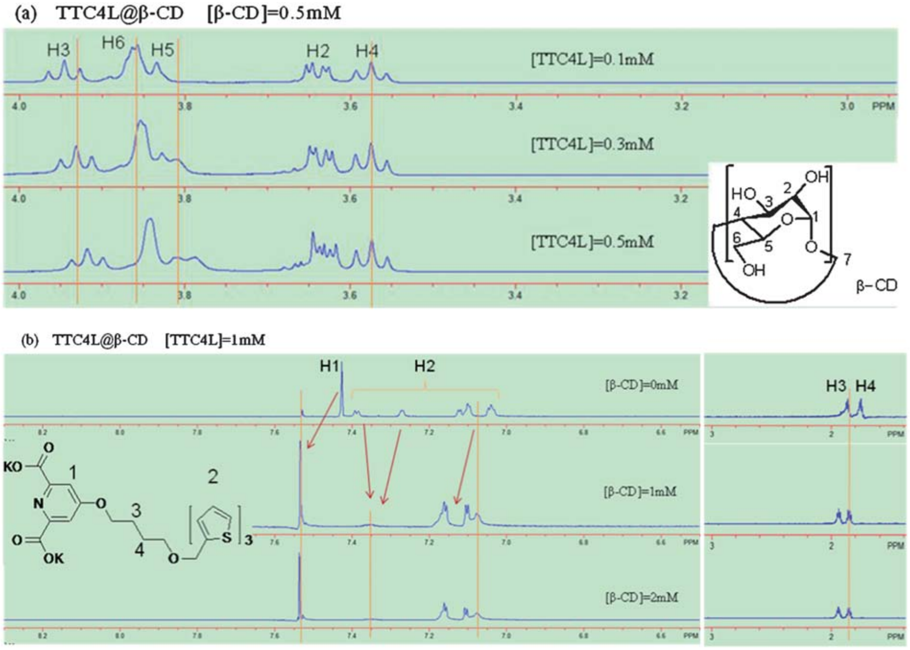


**Fig. 4** (a) $^{1}H$ NMR spectra (in $D_2O$) of β-CD upon addition of TTC4L. (b) $^{1}H$ NMR signals of TTC4L upon addition of β-CD.

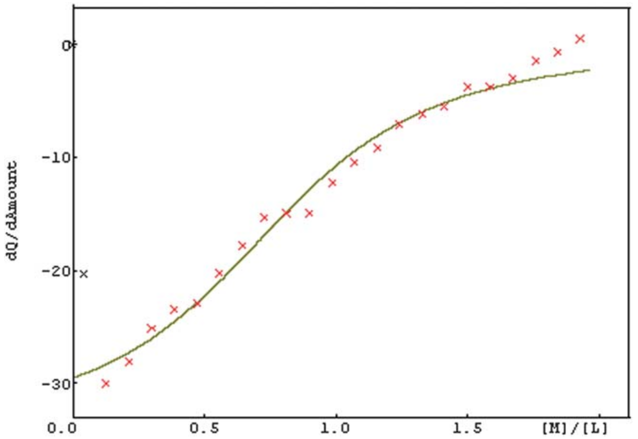
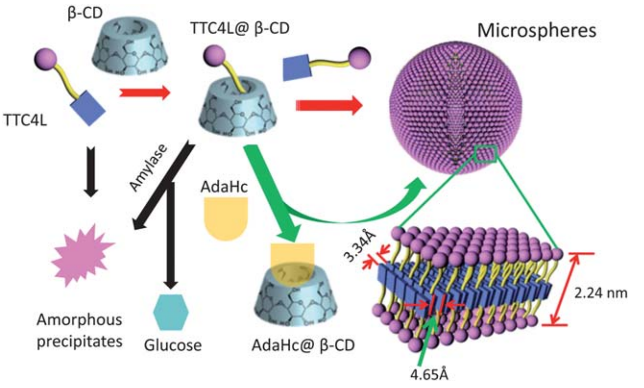


**Fig. 5** Thermal energy change with increasing the molar ratio of [β-CD]/[TTC4L]. [M] and [L] represent [β-CD] and [TTC4L], respectively. The solid line is the fitted results from the crosses that were obtained from experiment.



**Scheme 2** Proposed mechanism of the CD catalyzed molecular self-assembly of TTC4L into microspheres.

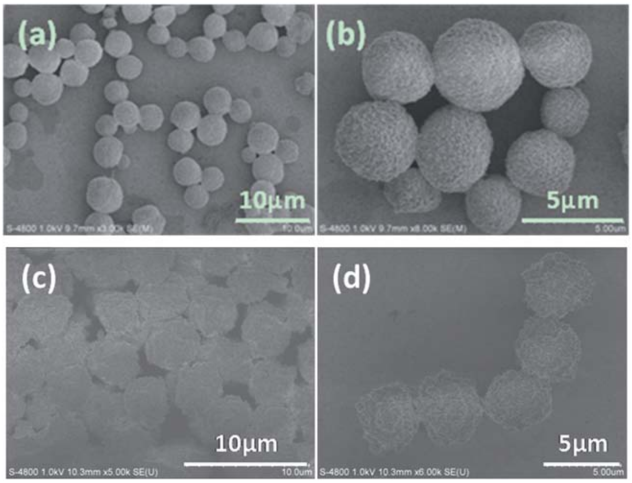


**Fig. 7** SEM images of microspheres formed in the TTC4L@HP-β-CD, 0.5 and 2 mM (a and b), and TTC4L@α-CD, 0.5 and 1.5 mM (c and d), systems.

of the C–O bond in COOH became stronger in the microspheres, which is characterized by the shift of its vibration from 1230 cm$^{-1}$ in the irregular precipitates to 1200 cm$^{-1}$ in the microspheres. The increase of the COOH component also leads to changes in the pyridine ring: the vibration of the pyridine skeleton at 1370 cm$^{-1}$ is considerably increased. Obviously, the microspheres are composed of more TTC4L in its acid form.

The absence of β-CD in the microspheres suggested that they behaved in a "catalytic" manner in the formation of the microspheres, namely they promoted the microsphere formation but remained in the supernate. To verify this, the yellowish supernate, a colour which indicates the presence of TTC4L, was separated and treated with α-amylase or 1-adamantanamine hydrochloride (AdaHC). The results are shown in Fig. 3. It is known that α-amylase can cleave α-1,4 linkages between the glucose units in CDs,[44–46] which will break the ring structure of CDs and produce glucose.[44] It is clear in Fig. 3a that upon incubating the supernate in an α-amylase environment, the turbidity of the system increases gradually, suggesting that insoluble TTC4L has been released. This implies that CDs were indeed in the supernate in the form of TTC4L@β-CD inclusion complexes. Upon addition of α-amylase, the ring structure of β-CD was decomposed so that free TTC4L was released. The released TTC4L molecules precipitate within 48 hours and the new supernate is transparent and colorless, suggesting a nearly complete precipitation of TTC4L. This is in clear contrast with

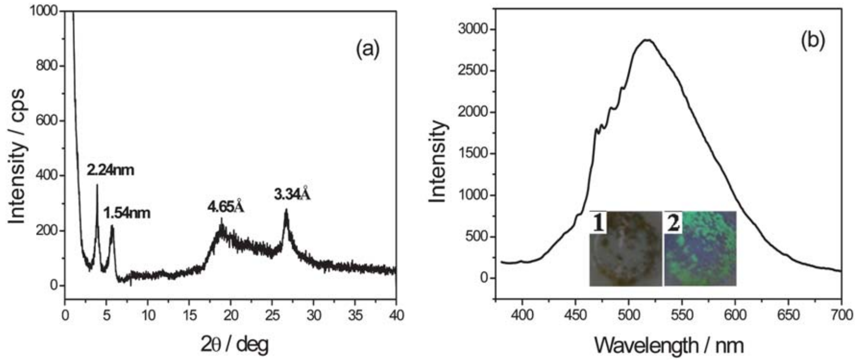


**Fig. 6** (a) XRD pattern of the TTC4L microspheres based on the TTC4L@β-CD system; (b) fluorescence emission spectrum of the TTC4L microspheres and photographs of the optical properties of the TTC4L microspheres: (1) under day light and (2) irradiated by 365 nm UV-light.

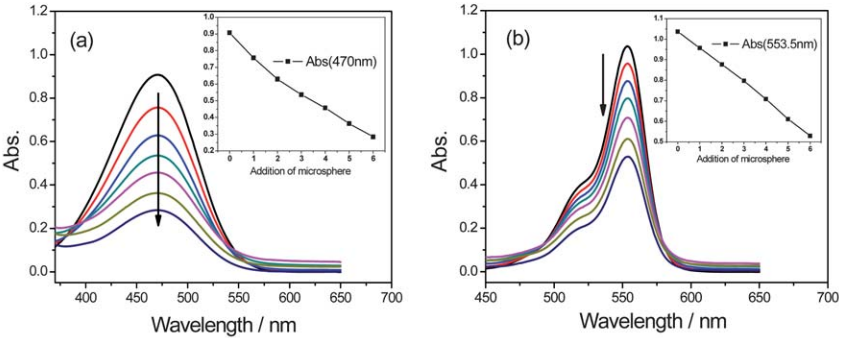


**Fig. 8** Absorption spectra of trans-4-styryl-1-methylpyridiniumiodide (SMP, a) and rhodamine B (RB, b) solutions along with the addition of microspheres. The inset graphs show the maximum absorbance of the absorption maxima, 470 nm and 553.5 nm, respectively.

the yellowish supernate in the β-CD free system, indicating that the acid form of TTC4L ($H_2A$) is almost insoluble in water, which is in good accordance with the pH titration results (Fig. S1†). SEM analysis reveals that the newly formed precipitates are irregular with few microspheres (Fig. 3b). Analogously, when AdaHC, a guest molecule that forms a more stable inclusion complex with β-CD,[42,47–49] was added to the original supernate, similar macroscopic phase behavior occurred (Fig. 3c). However, in this case, microspheres were observed (Fig. 3d). It should be noted that in both cases the pH is low enough to acidify the TTC4L molecules. The most striking difference lies in the final form of the β-CDs. In the former case, β-CDs were cleaved by α-amylase into glucose;[44] while in the latter β-CDs were still in the system. This strongly indicates that the formation of microspheres requires the presence of β-CD, and is not a simple result of lowering the chemical potential of the free TTC4L below the saturation value associated with the amorphous solid.

In order to get more insight into the role of β-CD on the microsphere formation, $^1H$ NMR measurements were performed on the TTC4L@β-CD inclusion complexes at various mixing ratios. We found that both the chemical shifts for TTC4L and β-CD changed noticeably (Fig. 4a), verifying the formation of an inclusion complex between them. It can be inferred from Fig. 4a that TTC4L and β-CD form 1 : 1 inclusion complexes since the chemical shifts didn't change further with a molar ratio beyond 1 : 1.

This 1 : 1 inclusion complex was further confirmed by ITC titration measurements (Fig. 5), and the binding constant was found to be $K = 1.3 \times 10^4 \pm 0.3 \times 10^4\ \mathrm{M}^{-1}$. This value of $K$ is of the same order, but is about 1/3 to 1/2 of that for conventional surfactant@β-CD inclusion complexes,[50,51] which means that the TTC4L binding is looser than that of a surfactant to β-CD. This is also reflected in the $^1H$ NMR results. The chemical shifts for $H_5$ (Fig. 4a) in the cavity of β-CD up-shifted by only 0.03 ppm upon inclusion, which is significantly lower than the typical chemical shifts in surfactant@β-CD systems.[52] The $^1H$ NMR spectra in Fig. 4b reveal that the chemical shifts for the protons on the terthiophene group have moved up field, suggesting that the binding site of TTC4L to β-CD is the terthiophene group. Meanwhile, the inclusion also causes an increased solvation degree of the TTC4L, so that the protons in the butyl and pyridine groups (Fig. 4b) shift downfield due to the increased environmental polarity.

According to Chem 3D modeling, we know that the extended length of the terthiophene group is about 11.1 Å, which is longer than the height of the torus of β-CD (7.9 Å). This implies that the terthiophene group cannot be hosted entirely in one β-CD cavity, so that π–π stacking may occur between the exposed terthiophenes in the TTC4L@β-CD complexes and the terthiophenes of the free TTC4L. However, the TTC4L@β-CD is easily replaced by another free TTC4L because the π–π stacking between two free TTC4L molecules is more stable and meets no hindrance from β-CD. It is expected that the exchange between TTC4L@β-CD and free TTC4L slows down the aggregation kinetics of TTC4L, so that they gain enough time to arrange in an ordered fashion to allow microsphere formation. As a matter of fact, the titration rate was found to be very crucial for the microsphere formation. Only slow pH titrations led to microspheres; fast precipitation always resulted in irregular precipitates. Nevertheless, β-CD is required to produce microspheres no matter how slow the titration rate is, suggesting that the inclusion complex of TTC4L@β-CD is involved in the microsphere formation process. Since the binding constant for TTC4L@β-CD is significantly smaller than that for surfactant@β-CD, an excess of β-CD is required to shift the binding equilibrium of TTC4L + β-CD toward TTC4L@β-CD inclusion complexes. As more TTC4L@β-CD is produced, the retarding effect on precipitation is expected to be stronger. That is why a much lower pH is needed to induce microsphere formation with an increasing concentration of β-CD (Fig. 1a).

The above catalytic mechanism also explains the fact that irregular precipitates formed when α-amylase was added to the TTC4L@β-CD supernate, whereas microspheres were fabricated by replacing α-amylase with AdaHc. In the former case, β-CD was destroyed by the α-amylase so that the released TTC4L stacked quickly due to the lack of disturbance. In contrast, in the later case, the newly produced free TTC4L molecules coexist with TTC4L@β-CD, so that the self-assembling process of TTC4L is disturbed which slows down the assembling kinetics and finally leads to microspheres. This also suggests that the TTC4L@β-CD complexes can be utilized to generate new microspheres in the presence of competitive guests. In this way, the catalyst can be recycled. The catalytic mechanism and the changes upon addition of α-amylase and AdaHc are schematically presented in Scheme 2.

The mode of molecular packing in the microspheres was examined by XRD measurements which reveal structural periodicity. For the TTC4L@β-CD microspheres prepared at 1 : 1, 1 : 3, and 1 : 5 molar ratios, the diffraction patterns are completely the same (Fig. 6a), and no characteristic β-CD signals[40] can be observed, in accordance with the elemental analysis results. The diffraction peaks at $2\theta = 3.94°$ and $5.74°$ correspond to $d_1 = 2.24$ nm and $d_2 = 1.54$ nm, respectively. The $d_1 : d_2 = \sqrt{2} : 1$ ratio suggests the presence of a cubic phase in the microspheres.[57] According to molecular modeling, the extended length of a pair of TTC4L molecules overlapping by their terthiophene moieties is about 2.3 nm, as illustrated in Scheme 2, which is in good agreement with the 2.24 nm distance obtained from XRD. The overlap between the terthiophene moieties can be verified from the diffraction peak at 26.7°, corresponding to the characteristic distance of π–π stacking (3.34 Å).[53,54] Meanwhile, the presence of a broad peak at 18.9° is in accordance with a distance of $d = 4.65$ Å. It is well established that oligothiophene moieties may form intermolecular excimers that are signified by a broad green-emission when the distance between the thiophenes is in the range of 4–7 Å.[55,56] Green fluorescence was indeed observed when the microspheres were irradiated with 365 nm UV light (inset in Fig. 6b). In Fig. 6b we show the fluorescence spectrum for the microspheres. Both the position and broad feature of the emissions are characteristics of thiophene excimers.[55]

As a control experiment, an XRD pattern of the irregular precipitates that were obtained without the presence of β-CD was also examined. It can be clearly observed in Fig. S4† that the diffraction peaks are different from that in Fig. 6a, suggesting that the TTC4L molecules arranged in a different way.

The above analysis suggested that the height of the CD cavity is the most important parameter that affects the packing between the TTC4L@CD inclusion complexes and the free TTC4L molecules. This means that CDs with various cavity diameters may all be employed for the generation of microspheres. This is indeed the case. In Fig. 7 we show that microspheres can be formed both with 2-hydroxypropyl substituted β-CD (HP-β-CD) and α-CD.

Finally, the microspheres were tested for the removal of an organic contaminant from water to utilize their surface roughness. In Fig. 8 it can be clearly seen that upon addition of microspheres into dye-contaminated water, the absorption from the dyes decreased drastically. It should be noticed that these microspheres are very efficient in treating positively charged contaminated water, because they are negatively charged (zeta potential ~ −20 mV).

## Conclusions

In summary, we have established a case of cyclodextrin-catalyzed molecular self-assembly in this work. CDs may assist the strongly hydrophobic amphiphile TTC4L self-assemble into ordered structures instead of forming amorphous precipitates. By inclusion with CDs, TTC4L can assemble into microspheres, whereas CDs remain in the supernate in the form of soluble TTC4L@CD inclusion complexes. The TTC4L@CD inclusion complexes may be used to generate extra microspheres and the catalyst can be recycled in the presence of competitive guests. As well as β-CD, α-CD and HP-β-CD may behave similarly in 'catalyzing' microsphere formation in these TTC4L systems. We expect that this study will serve as a corner stone for CD-catalyzed self-assembly and open a new vista for fabricating state-of-the-art materials.

## Acknowledgements

This research was supported by National Natural Science Foundation of China (21173011, 51121091, 21073006), 973 Program (2013CB933800), and Doctorial Fund of Ministry of Education of China.

## References

1 M. A. Mateos-Timoneda, M. Crego-Calama and D. N. Reinhoudt, *Chem. Soc. Rev.*, 2004, **33**, 363–372.

2 S. Vauthey, S. Santoso, H. Y. Gong, N. Watson and S. G. Zhang, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5355–5360.

3 C. Li, M. Numata, A.-H. Bae, K. Sakurai and S. Shinkai, *J. Am. Chem. Soc.*, 2005, **127**, 4548–4549.

4 J. H. Fendler, *Chem. Mater.*, 1996, **8**, 1616–1624.

5 S. Zhang, *Nat. Biotechnol.*, 2003, **21**, 1171–1178.

6 J. A. A. W. Elemans, R. van Hameren, R. J. M. Nolte and A. E. Rowan, *Adv. Mater.*, 2006, **18**, 1251–1266.

7 A. Blanazs, S. P. Armes and A. J. Ryan, *Macromol. Rapid Commun.*, 2009, **30**, 267–277.

8 T. Wink, S. J. van Zuilen, A. Bult and W. P. van Bennekom, *Analyst*, 1997, **122**, 43–50.

9 W. T. Truong, Y. Su, J. T. Meijer, P. Thordarson and F. Braet, *Chem.–Asian J.*, 2011, **6**, 30–42.

10 D. Chandler, *Nature*, 2005, **437**, 640–647.

11 L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem., Int. Ed.*, 2001, **40**, 2382–2426.

12 J. H. Ryu, D. J. Hong and M. Lee, *Chem. Commun.*, 2008, 1043–1054.

13 Y. Yan and J. B. Huang, *Coord. Chem. Rev.*, 2010, **254**, 1072–1080.

14 E. Kaler, A. Murthy, B. Rodriguez and J. Zasadzinski, *Science*, 1989, **245**, 1371–1374.

15 A. O'Riordan, P. Delaney and G. Redmond, *Nano Lett.*, 2004, **4**, 761–765.

16 H. G. Cui, E. T. Pashuck, Y. S. Velichko, S. J. Weigand, A. G. Cheetham, C. J. Newcomb and S. I. Stupp, *Science*, 2010, **327**, 555–559.

17 Z. Y. Zheng, K. Y. Gao, Y. H. Luo, D. M. Li, Q. B. Meng, Y. R. Wang and D. Z. Zhangt, *J. Am. Chem. Soc.*, 2008, **130**, 9785–9789.

18 J. Wang, Q. W. Chen, C. Zeng and B. Y. Hou, *Adv. Mater.*, 2004, **16**, 137–138.

19 B. G. Kim, M. S. Kim and J. Kim, *ACS Nano*, 2010, **4**, 2160–2166.

20 H. W. Duan, D. Y. Chen, M. Jiang, W. J. Gan, S. J. Li, M. Wang and J. Gong, *J. Am. Chem. Soc.*, 2001, **123**, 12097–12098.

21 J. Ruokolainen, R. Makinen, M. Torkkeli, T. Makela, R. Serimaa, G. ten Brinke and O. Ikkala, *Science*, 1998, **280**, 557–560.

22 Q. An, Q. Chen, W. Zhu, Y. Li, C. A. Tao, H. W. Yang, Z. P. Li, L. J. Wan, H. Tian and G. T. Li, *Chem. Commun.*, 2010, **46**, 725–727.

23 H. Li, X. Xu, J. Shang, J. Li, X. Hu, B. K. Teo and K. Wu, *J. Phys. Chem. C*, 2012, **116**, 21753–21761.

24 H. Shiozawa, B. C. S. Chia, N. L. Davies, R. Zerella and D. H. Williams, *J. Am. Chem. Soc.*, 2002, **124**, 3914–3919.

25 S. H. Um, J. B. Lee, N. Park, S. Y. Kwon, C. C. Umbach and D. Luo, *Nat. Mater.*, 2006, **5**, 797–801.

26 H. X. L. Y. Wang, S. Y. Ding, D. Y. Liu, L. Chen, Z. C. Lei, F. R. Fan and Z. Q. Tian, *Sci. Sin.: Chim.*, 2012, **42**, 525–547.

27 W. S. Jeon, K. Moon, S. H. Park, H. Chun, Y. H. Ko, J. Y. Lee, E. S. Lee, S. Samal, N. Selvapalam, M. V. Rekharsky, V. Sindelar, D. Sobransingh, Y. Inoue, A. E. Kaifer and K. Kim, *J. Am. Chem. Soc.*, 2005, **127**, 12984–12989.

28 M. V. Rekharsky and Y. Inoue, *Chem. Rev.*, 1998, **98**, 1875–1917.

29 L. X. Jiang, Y. Yan and J. B. Huang, *Adv. Colloid Interface Sci.*, 2011, **169**, 13–25.

30 Y. Yan, L. X. Jiang and J. B. Huang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9074–9082.

31 R. Liu, Y. Zhang and P. Y. Feng, *J. Am. Chem. Soc.*, 2009, **131**, 15128–15129.

32 N. M. Khashab, A. Trabolsi, Y. A. Lau, M. W. Ambrogio, D. C. Friedman, H. A. Khatib, J. I. Zink and J. F. Stoddart, *Eur. J. Org. Chem.*, 2009, 1669–1673.

33 L. X. Jiang, Y. Yan, J. B. Huang, C. F. Yu, C. W. Jin, M. L. Deng and Y. L. Wang, *J. Phys. Chem. B*, 2010, **114**, 2165–2174.

34 T. Taira, Y. Suzaki and K. Osakada, *Chem. Commun.*, 2009, 7027–7029.

35 C. Park, I. H. Lee, S. Lee, Y. Song, M. Rhue and C. Kim, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 1199–1203.

36 P. B. Wan, Y. G. Jiang, Y. P. Wang, Z. Q. Wang and X. Zhang, *Chem. Commun.*, 2008, 5710–5712.

37 Y. P. Wang, N. Ma, Z. Q. Wang and X. Zhang, *Angew. Chem., Int. Ed.*, 2007, **46**, 2823–2826.

38 G. M. Nicolle and A. E. Merbach, *Chem. Commun.*, 2004, 854–855.

39 W. Tao, Y. Liu, B. B. Jiang, S. R. Yu, W. Huang, Y. F. Zhou and D. Y. Yan, *J. Am. Chem. Soc.*, 2012, **134**, 762–764.

40 L. X. Jiang, Y. Peng, Y. Yan, M. L. Deng, Y. L. Wang and J. B. Huang, *Soft Matter*, 2010, **6**, 1731–1736.

41 L. X. Jiang, Y. Peng, Y. Yan and J. B. Huang, *Soft Matter*, 2011, **7**, 1726–1731.

42 L. X. Jiang, Y. Yan and J. B. Huang, *Soft Matter*, 2011, **7**, 10417–10423.

43 L. Zhao, X. H. Cheng, Y. Ding, Y. Yan and J. B. Huang, *Soft Matter*, 2012, **8**, 10472–10478.

44 L. X. Jiang, Y. Yan, M. Drechsler and J. B. Huang, *Chem. Commun.*, 2012, **48**, 7347–7349.

45 C. Park, H. Kim, S. Kim and C. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 16614–16615.

46 S. Mahammad, A. Abdala, G. W. Roberts and S. A. Khan, *Soft Matter*, 2010, **6**, 4237–4245.

47 Y. Xu, S. Bolisetty, M. Ballauff and A. H. E. Muller, *J. Am. Chem. Soc.*, 2009, **131**, 1640–1641.

48 G. Chen and M. Jiang, *Chem. Soc. Rev.*, 2011, **40**, 2254–2266.

49 T. Ogoshi, Y. Takashima, H. Yamaguchi and A. Harada, *J. Am. Chem. Soc.*, 2007, **129**, 4878–4879.

50 H. Mwakibete, R. Cristantino, D. M. Bloor, E. Wynjones and J. F. Holzwarth, *Langmuir*, 1995, **11**, 57–60.

51 L. X. Jiang, C. F. Yu, M. L. Deng, C. W. Lin, Y. L. Wang, Y. Yan and J. B. Huang, *J. Phys. Chem. B*, 2010, **114**, 4937.

52 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.

53 S. Saito, K. Nakakura and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2012, **51**, 714–717.

54 M. R. Molla and S. Ghosh, *Chem.–Eur. J.*, 2012, **18**, 1290–1294.

55 W. Mroz, J. P. Bombenger, C. Botta, A. O. Biroli, M. Pizzotti, F. De Angelis, L. Belpassi, R. Tubino and F. Meinardi, *Chem.–Eur. J.*, 2009, **15**, 12791–12798.

56 M. Fujitsuka, D. W. Cho, J. Ohshita, A. Kunai and T. Majima, *J. Phys. Chem. C*, 2007, **111**, 1993–1998.

57 R. Ziessel, G. Pickaert, F. Camerel, B. Donnio, D. Guillon, M. Cesario and T. Prange, *J. Am. Chem. Soc.*, 2004, **126**, 12403–12413.