Electronic supplementary information (ESI)

β-Cyclodextrin induced hierarchical self-assembly of a cationic surfactant bearing an adamantane end group in aqueous solution

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Synthesis of 1-[11-((adamantane-1-carbonyl)oxy)undecyl]pyridinium Bromide.

Materials. 1-adamantanecarboxylic acid (98%) and 11-bromo-1-undecanol (99%) were purchased from Beijing HWRK Chem. Co., LTD. The other chemicals were of analytical grade. All of them were used as received without further purifications.

Synthesis of 1-adamantanecarboxylic Acid Chloride. The oxalyl chloride (3.4 mL) was dropwise added to a solution of 1-adamantanecarboxylic acid (1.8 g) in dry CH_2Cl_2 (20 mL) with stirring under a N_2 atmosphere in an ice-bath. After stirring for 2 hours at room temperature, the solution was evaporated in vacuum. The product was used immediately in the next step.

Synthesis of 11-Bromoundecyl Adamantane-1-carboxylate. To a mixture solution of 11-bromo-1-undecanol (5.0 g) and triethylamine (2.8 mL) in dry THF (40 mL) was dropwise added a solution of 1-adamantanecarboxylic acid chloride in dry THF (10 mL) with stirring under nitrogen atmosphere for 24 hours. After evaporation of the solvent, the crude product was purified using silica gel column chromatography. The effluent was CH_2Cl_2/PE = 1:1. The product purity was ascertained by nuclear magnetic resonance spectroscopy (^{1}H NMR) in $CDCl_3$. ^{1}H NMR: (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 4.03 (2 H, t, CH_2O), 3.41 (2 H, t, NCH_2), 2.01(2 H, m, CH_2), 1.85(3 H, s, CH), 1.82(6 H, s, CH_2), 1.69(6 H, s, CH_2), 1.60(2 H, m, CH_2), 1.25~1.45 (14 H, m, CH_2).

Synthesis of 1-[11-((adamantane-1-carbonyl)oxy)undecyl]pyridinium Bromide. The 11-bromoundecyl adamantane-1-carboxylate (5.8 g) and pyridine (150 mL) were refluxed in acetone (50 mL) in a 500 mL flask for 2 days under nitrogen atmosphere. The excess pyridine and acetone were removed by vacuum evaporation. The residue was purified by recrystallization with methanol and diethyl ether twice. The product purity was ascertained by ^{1}H NMR, high-revolution mass spectrometry (HR-MS) in D_2O and elemental analysis. ^{1}H NMR: (300 MHz, D_2O, 25 °C): δ (ppm) 8.93 (2 H, d, pyridine-H), 8.53 (1 H, t, pyridine-H), 8.05 (2 H, t, pyridine-H), 4.62 (2 H, t, CH_2O), 3.83(2 H, t, NCH_2), 1.92(2 H, m, CH_2), 1.78(3 H, s, CH), 1.67(6 H, s, CH_2), 1.51(6 H, s,

CH_2), 1.41(2 H, m, CH_2), 1.08~1.25 (14 H, m, CH_2). HR-MS (ESI): M/Z calc. for $C_{27}H_{42}NO_2^+$: 412.5968; found, 412.5916. Elemental analysis calc. (%) for $C_{27}H_{42}NO_2Br$: C: 65.72, H: 8.37, N: 2.76; found: C 65.85, H 8.59, N 2.84.

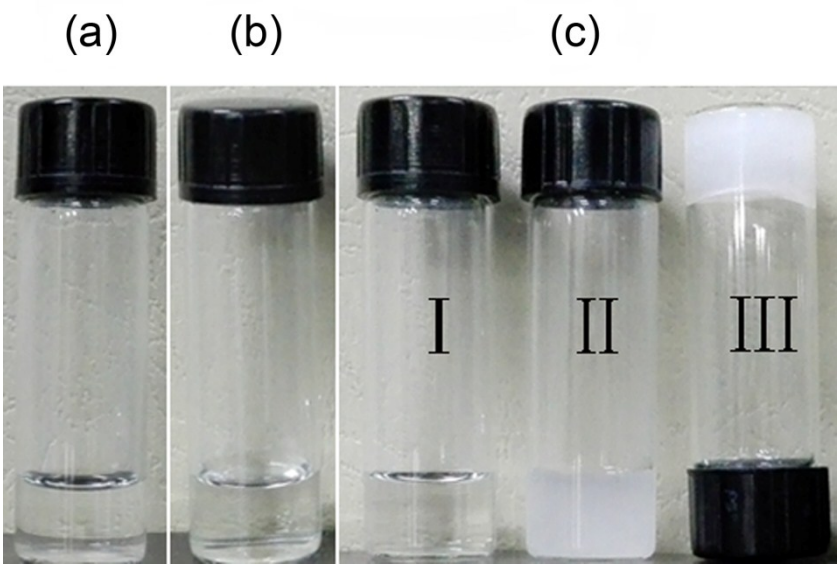

Fig. S1 Representative sample appearance images of AP (60 mM) (a), AP@1β-CD (60 mM) (b) and AP@2β-CD (c) at different concentrations: (I) 20 mM, (II) 50 mM, (III) 70 mM.

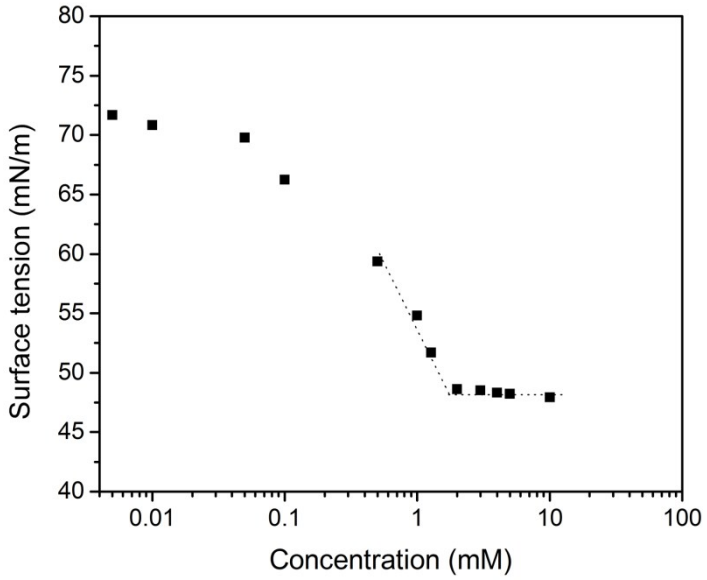

Fig. S2 Surface tension curve of AP in aqueous solution at 25 °C.

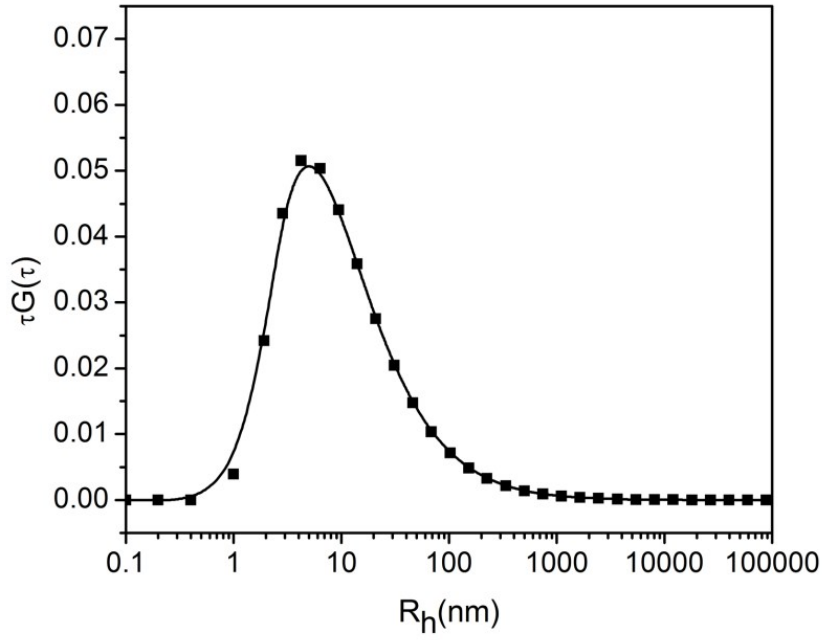

Fig. S3 Hydrodynamic radius (R_h) distribution of aggregates formed in 60 mM AP aqueous solution determined by DLS at 25 °C.

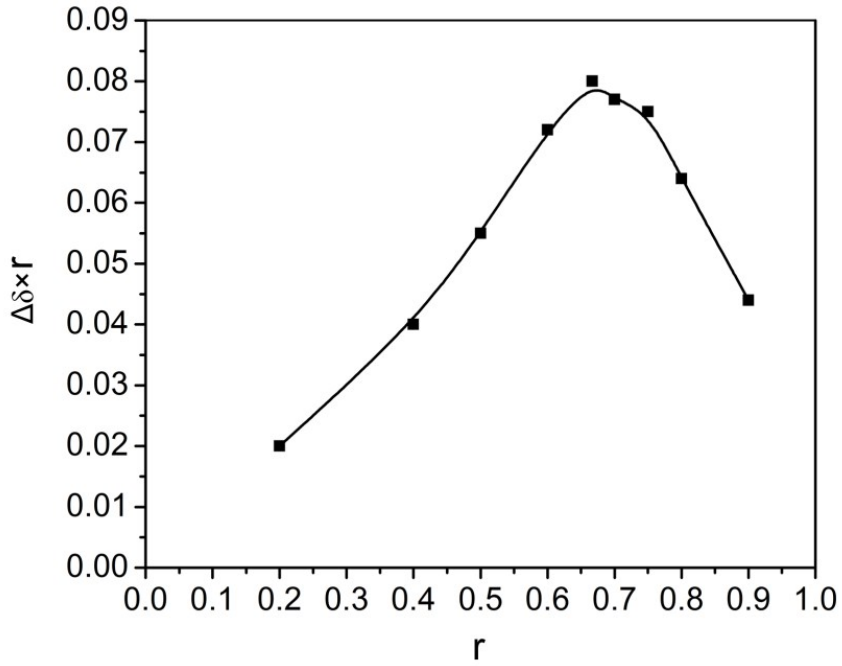

Fig. S4 ^{1}H NMR Job's plot corresponding to the chemical shift of H-5 of β-CD in D_2O. [AP]+[β-CD] =15 mM.

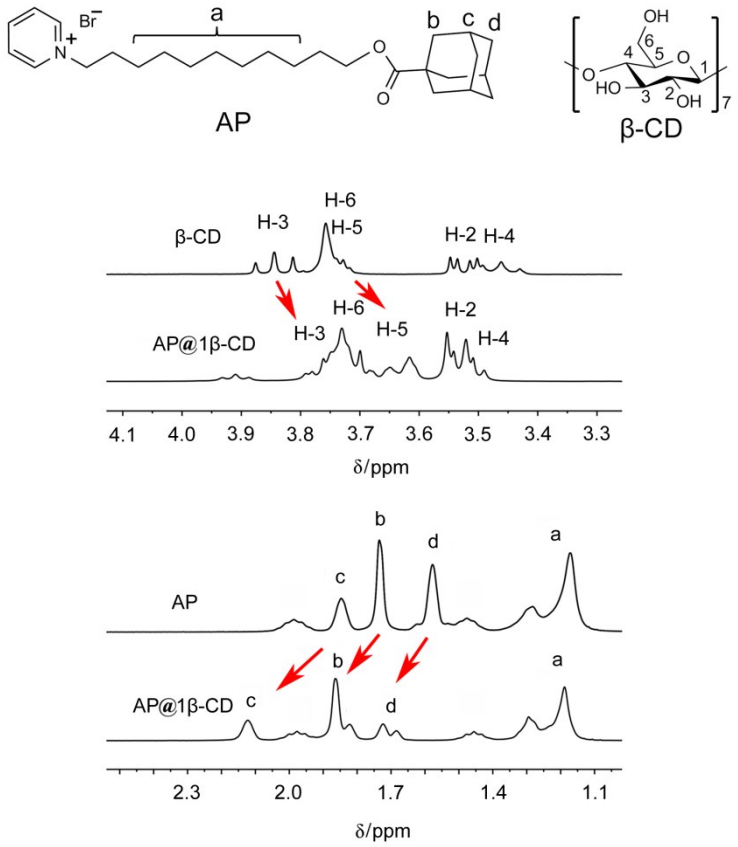

Fig. S5 Chemical structures of AP and β-CD with their individual ^{1}H NMR spectra for comparison with that at a β-CD:AP molar ratio of 1:1 in D_2O at 25 °C.

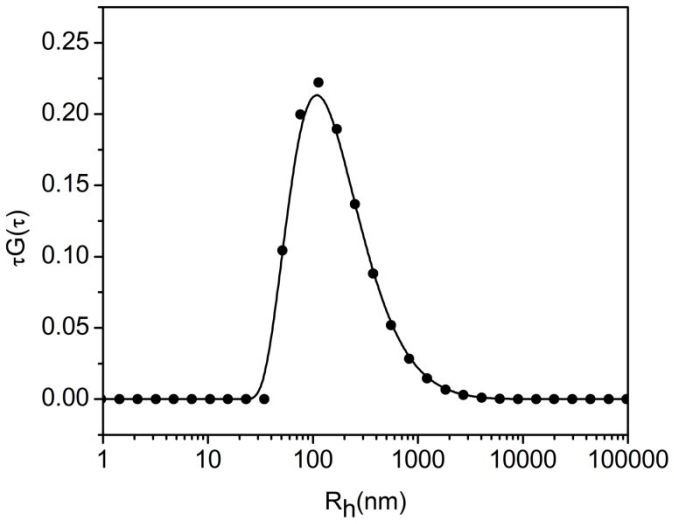

Fig. S6 DLS result of 60 mM AP@1β-CD in aqueous solution at 25 °C.

In order to verify that the vesicles were formed by AP@1β-CD inclusions rather than by β-CD itself, the microstructure of aggregates in the β-CD aqueous solution was studied. As shown in Fig.

S8, the aggregates presented a polygonal appearance and seem to adhere to each other to form larger aggregates, which was in line with literature reports.[1,2] In addition, according to the strong binding ability with an association constant around 10^5 M^{-1} of β-CD and adamantane, the concentration of free β-CD molecules was far less than its critical aggregation concentration (3 mM) in water. This suggested that the aggregates observed in the mixed samples were resulted from the self-assembly of AP@1β-CD inclusion complexes.

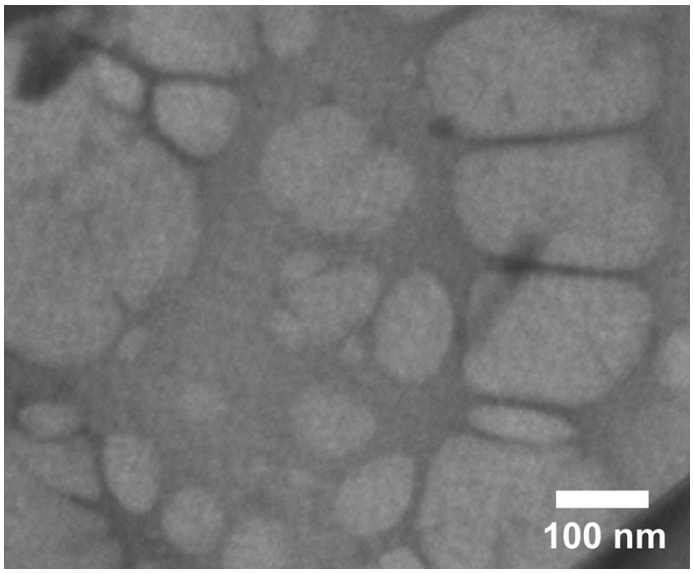

Fig. S7 TEM micrograph for 6 mM β-CD in aqueous solution.

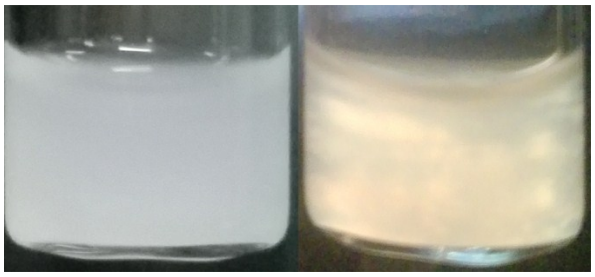

Fig. S8 The visual appearance photo of 50 mM AP@2β-CD sample without (A) or under (B) the crossed polarizers at 25 °C.

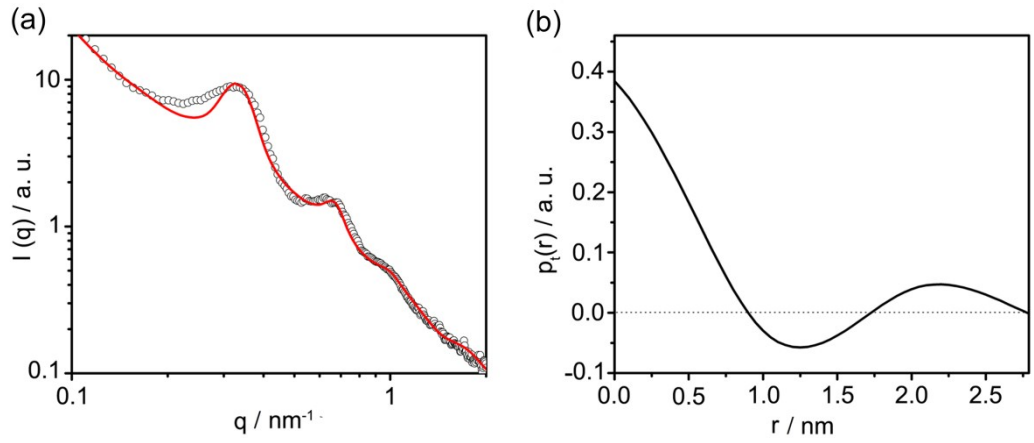

Fig. S9 (a) Normalized SAXS profile for the sample from AP@2β-CD at 50 mM; where the circles and dots represent respectively the experimental data and the GIFT fitting curve and (b) the corresponding p(r) profile.

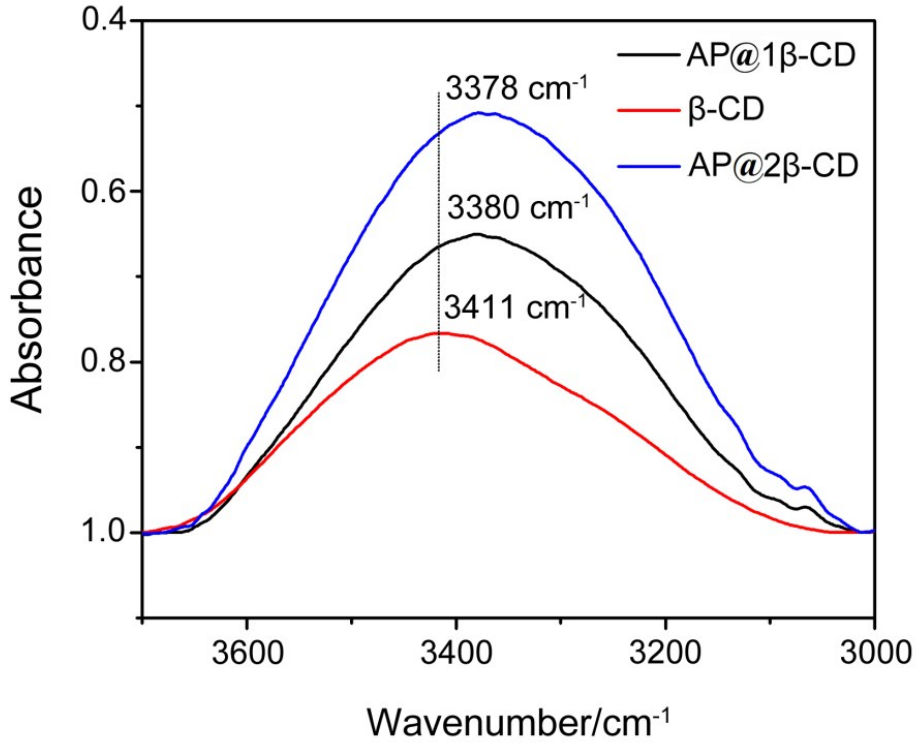

Fig. S10 FTIR results for the hydroxyl group of β-CD, AP@1β-CD (70mM), AP@2β-CD (70 mM).

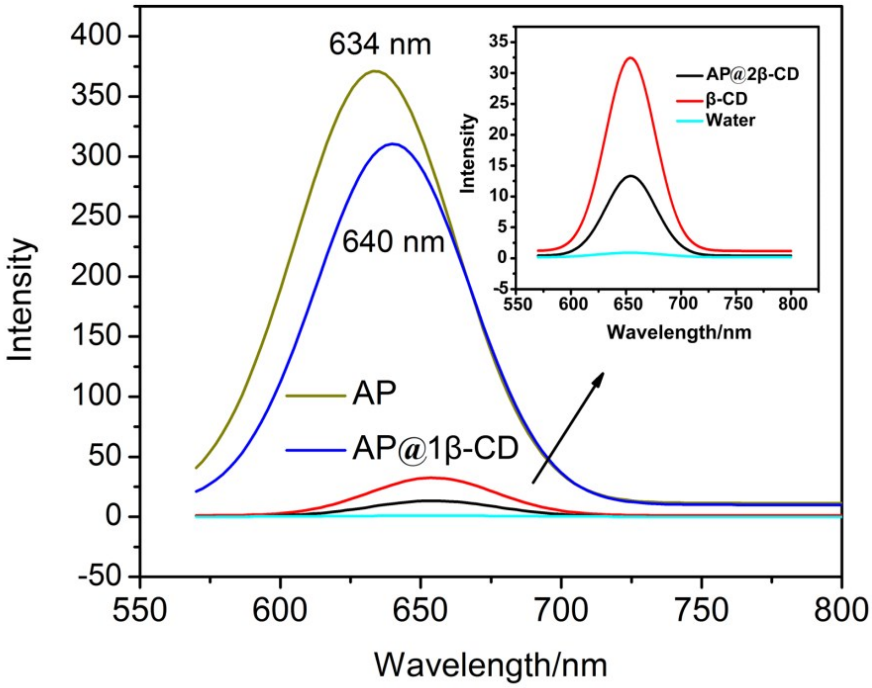

Fig. S11 Fluorescence emission spectra of Nile red in water and aqueous solutions of AP (5 mM), β-CD (5 mM), AP@1β-CD (60 mM), AP@2β-CD (50 mM) with the excitation wavelength at 550 nm at 25 °C. The inset was the amplified spectra Nile red in water, β-CD and AP@2β-CD.

References

1. B. Massimo, R. Simona, K. Göran, A. Mats, L. N. Pierandrea and B. Piero, *Langmuir,* 2006, **22,** 1478-1484.

2. X. Yue, X. Chen and Q. T. Li, *Colloid Surface A*，2015, **482,** 79-86.