Electronic Supplementary Material (ESI) for Polymer Chemistry.

Morphology Transitions of Supramolecular Hyperbranched Polymers Induced by Double Supramolecular Driving Forces

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1 Synthesis of alkynyl-terminated Ada, Ada-alk$_2$

Ada-NH_2 (756 mg, 5 mmol), K_2CO_3 (5520 mg, 40mmol) and Propargylbromide (4462 mg, 30 mol) were dissolved in dry DMF (30mL). After being bubbled with nitrogen gas for 30 min, the reaction was conducted at 60 °C for 48 hours. After removing the insoluble salts by suction filtration, the filtrate was concentrated and then further purified by silica gel column chromatography using petroleum ether/ethyl acetate

(1:1 v/v) as the eluent. After removing the solvent by a rotary evaporator, the obtained residue was distilled under reduced pressure. Yield: 78%.. Yield: 75.3%. FT-IR (KBr): 3256cm^{-1} (ν, ≡C-H); 2103cm^{-1} (ν, C≡C). ^{1}H NMR ($CDCl_3$, TMS): δ= 1.52-2.15 (15H, Ada); 2.41(1H,-C≡CH); 3.32 (2H, -CH_2C≡CH).

2 Synthesis of Ada-CD_2

The synthesis of Ada-CD_2 was accomplished by click reaction between Ada-alk_2 and *β*-CD-N_3. At first, a mixture of *β*-CD-N_3 (877 mg, 0.76 mmol), Ada-alk_2 (78 mg, 0.34 mmol) and DMF (6 mL) was bubbled with nitrogen gas for 15 min. Cu(PPh_3)$_3$Br (130.2 mg, 0.14 mmol) was then added into the reaction system. After being bubbled with nitrogen gas for 30 min, the reaction was conducted at 60 °C for 18 hours, and then, Alk-wang resin (500 mg) was added and allowed this system to react for another 8 hours under nitrogen atmosphere. The mixture was exposed to air and diluted with DMF, followed by passing it through a neutral Al_2O_3 column, and then, subjected to rotary evaporation. The residue was precipitated into cold acetone and washed with acetone three times. Finally, the product was dried under vacuum at 30 °C for 1 day. Yield: 80%。FT-IR (KBr): 3370cm^{-1} (ν,O-H); 2870cm^{-1} (ν,C-H); 1033cm^{-1} (ν, C-O-C in *β*-CD). ^{1}H NMR (DMSO-d_6, TMS): δ=1.45-2.1 (15H, Ada); 3.95-3.2 (2,3,4,5,6-H in *β*-CD); 4.6-4.3 (12H, 6-OH); 4.98-

4.7 (14H, 1-H); 5.9–5.6 (28H, 2,3-OH); δ=8.02 (2H, methine proton in 1,2,3-triazole).

3 Characterization of Ada-CD_2

Fourier Transform Infrared (FT-IR) spectra were recorded on a NICOLET iS10 IR spectrometer. The ^{1}H NMR spectra were obtained from a Bruker Avance 300 spectrometer (Bruker BioSpin, Switzerland) operating at 300 MHz (1H) in $CDCl_3$ or DMSO-d_6. The 2D ^{1}H NMR ROESY spectra were recorded on a Bruker-Avance III NMR spectrometer (400 MHz) with D_2O/DMSO-d_6 as solvent. The molecular structure parameters of the polymer synthesized were determined on a Q-TOF-MS, measurements were performed on a Waters-ACQUITYTM UPLC & Q-TOF-MS Premier with deionized water as the solvent.

4 Results and Discussion

The amphiphilic AB_2 monomer Ada-CD_2 was first synthesized to study its supramolecular behaviors in varied solvents according to the routes depicted in Scheme 1. To enhance the functionality of Ada-NH_2, two alkyne units were introduced into its ends by the alkylation reaction in the presence of K_2CO_3, which is denoted as Ada-alk_2. In the FT-IR spectrum of Ada-alk_2 (Fig. S1(a)), the appearance of the characteristic absorption peak of alkynyl at 3256 cm^{-1}, 2103 cm^{-1} demostrated that the amino group in adamantane have reacted with propargylbromide. That was also evidenced by the appearance of proton peaks a and d in the ^{1}H

NMR spectrum of Ada-alk$_2$ (Fig. S2-(Ⅱ)). The peak integral ratio of proton **d** to **a** was calculated to be 1.94, and the signal of proton **a** in amino group disappeared, these results mentioned demonstrated that the alkylation reaction could be completly proceeded.

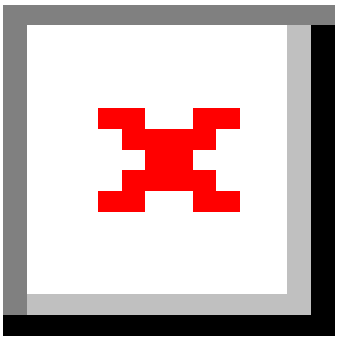

Figure. S1 FT-IR spectra of alkynyl-terminated Ada, Ada-alk$_2$ (a) and AB$_2$ type monomer, Ada-CD$_2$ (b).

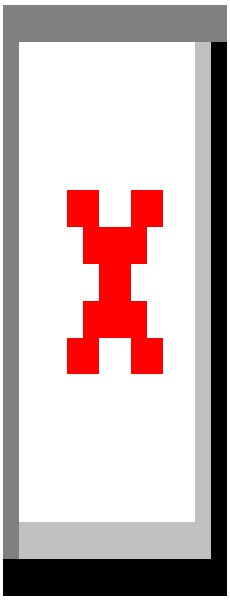

Figure. S2 ^{1}H NMR spectra of the Ada-NH_2(Ⅰ),Ada-alk_2(Ⅱ) and Ada-CD_2 (III).

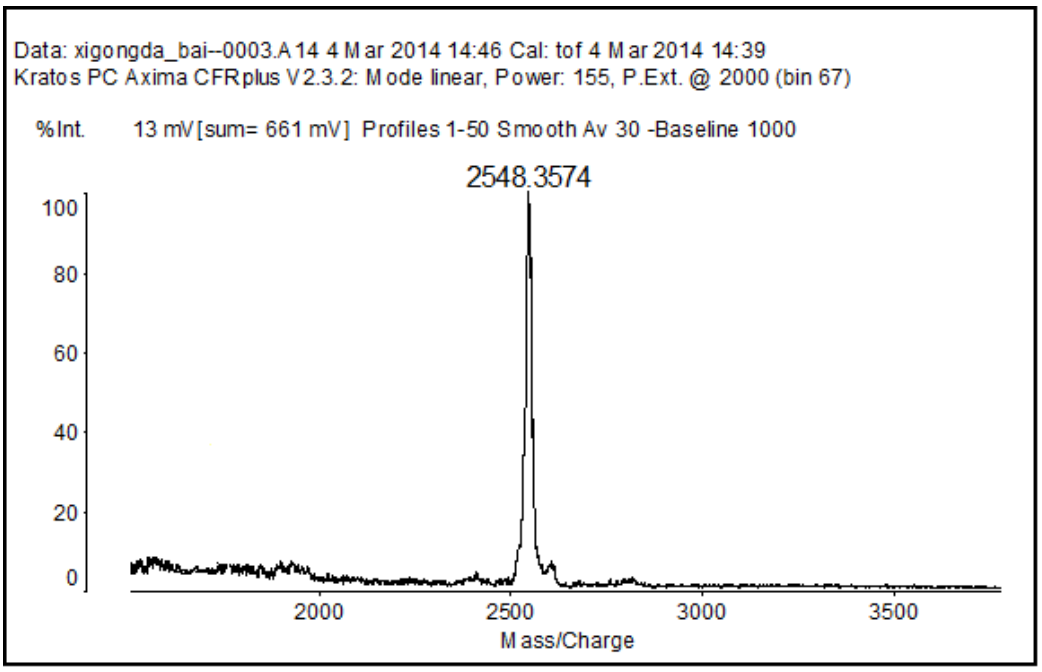

Figure. S3 MALDI-TOF-MS spectrum of Ada-CD_2

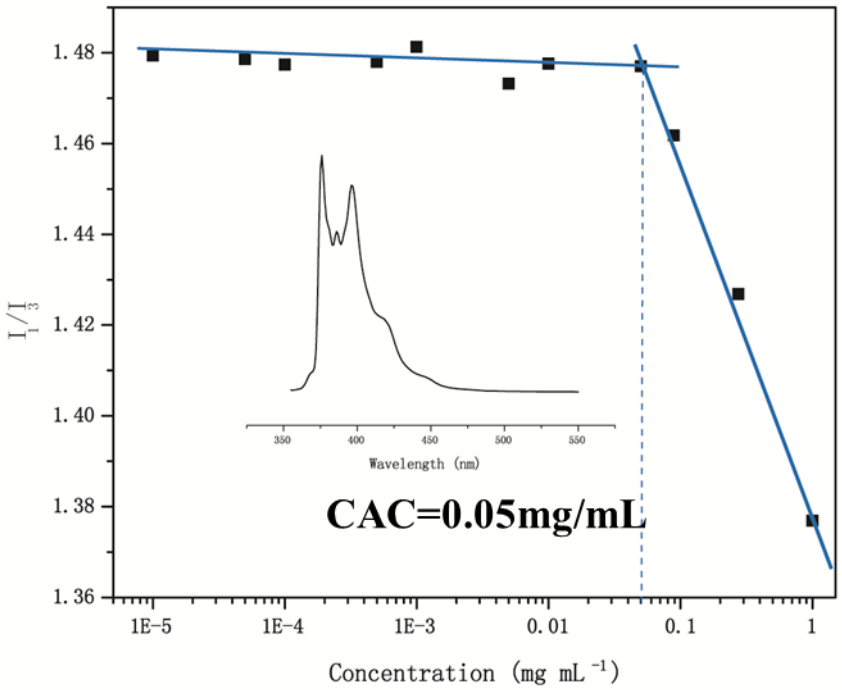

Figure. S4 Relationship between the fluorescence intensity ratio and the Ada-CD_2 concentration in DMF/H_2O (1:2) solutions after the addition of Ada-Na at 25 °C (inset: the pyrene fluorescence emission spectrum).

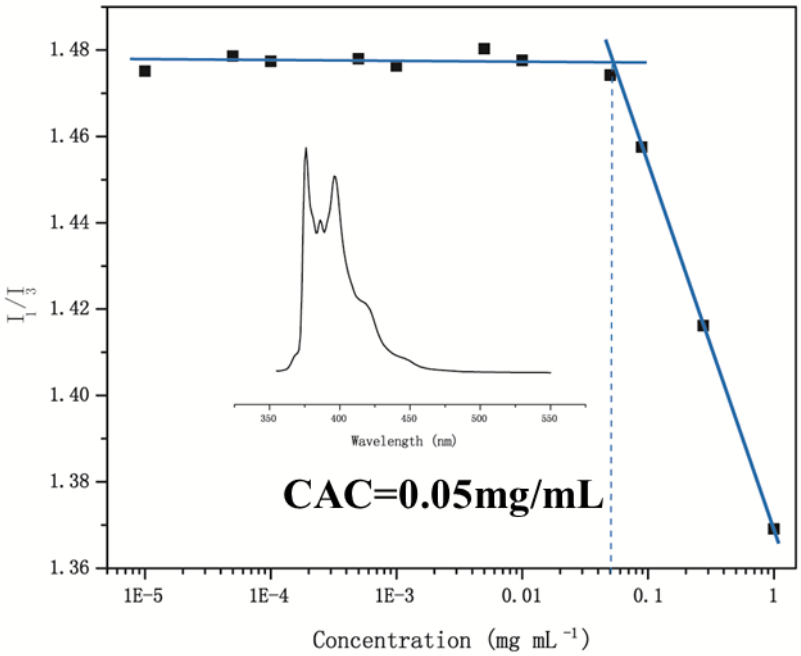

Figure. S5 Relationship between the fluorescence intensity ratio and the Ada-CD_2 concentration in DMF/H_2O (2:1) solutions after the addition of Ada-Na at 25 °C (inset: the pyrene fluorescence emission spectrum).