Supporting Information

Self-Assembly Morphology-Tunable Single Component Supramolecular Antibiotic for Enhanced Antibacterial Manipulation

Xin Song†[a], Xudong Deng†[b], Qinghua Wang†[c], Jinjin Tian[a], Feng-Li He[b], Hai-Yu Hu[c], and Wei Tian*[a]

[a] *MOE Key Laboratory of Material Physics and Chemistry under Extraordinary Conditions and Shanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an, 710072, Shaanxi, P. R. China E-mail: happytw_3000@nwpu.edu.cn*

[b] *Key Laboratory for Space Bioscience and Biotechnology, School of Life Sciences, Northwestern Polytechnical University, Xi'an 710072, Shaanxi, P. R. China.*

[c] *State Key Laboratory of Bioactive Substances and Function of Natural Medicine, and Beijing Key Laboratory of Active Substances Discovery and Drugability Evaluation, Institute of Materia Medica, Peking Union Medical College and Chinese Academy of Medical Sciences, Beijing 100050, P. R. China*

[†] These authors contributed equally to this work.

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1. Materials and methods

1.1 Materials

Propargylamine, tetrabutylammonium bromide and 1-dodecanethiol were purchased form Aladdin Reagents, China. Bis(triphenylphosphine)palladium(II) chloride, 4-iodoaniline, ethynyltrimethylsilane, and 1-bromododecane were purchased form TCI, Japan. EDC·HCl, 4-dimethylaminopyridine (DMAP), CuI and bromopropionic acid were purchased form J&K Scientific Ltd, China. N,N-dimethylaminoethyl acrylate (DMAEA), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), *p*-toluenesulfonyl chloride (TsCl) and TBAF (1M in THF) were purchased form Adamas, China. CuBr was purchased form Macklin and purified by washing with acetic acid and methanol before use. β-cyclodextrin (β-CD) was purchased from the Tianjin Kermel Chemical Reagents Development Center (China), and was recrystallized in water for purification. Other chemical reagents were purchased from Inno-Chem, China. Inorganic salts and organic solvents were purchased from Tianjin Kermel Chemical Reagents Development Center. Organic solvents were dried with 4 Å grade molecular sieves before use. All agents were used as received unless special statement.

1.2 Structure characterization methods

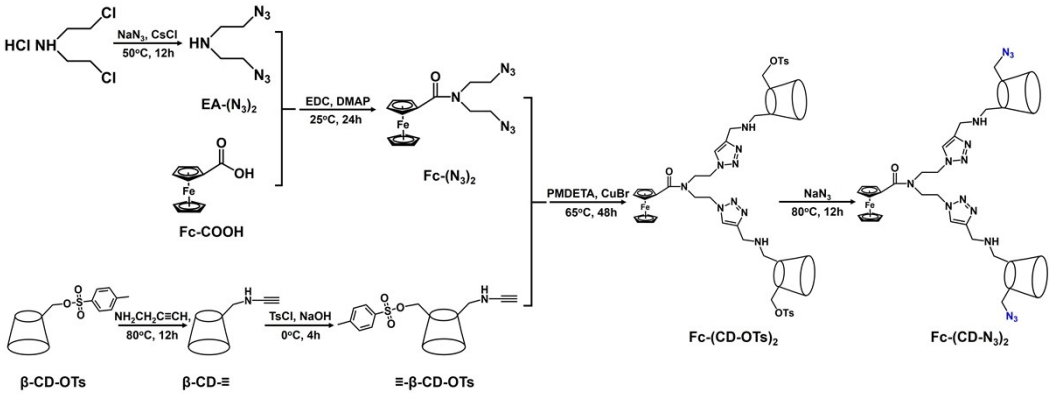
^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance 400MHz spectrometer (Bruker BioSpin, Switzerland) dissolved in $CDCl_3$, DMSO-d_6 or D_2O as the solvents. The 2D NOESY spectra were measured on a Bruker Avance 600MHz spectrometer (Bruker BioSpin, Switzerland) dissolved in D_2O as the solvent. The fluorescence spectrum was recorded by fluorescence spectroscopy (Hitachi F-4600). Electrospray Ionization Mass Spectrometry were obtained using a micro TOF-Q Ⅱ 10280 (Varian Inc., USA) with suitable solvent. MALDI-TOF-MS measurements were performed on a Bruker-Autoflex III & MALDI-TOF-MS. The molecular weight of polymers was recorded by the SEC-MALLS model, and chosen DMF as solvents.

1.3 Self-assembly behavior characterization methods

Particle size and zeta potent of each self-assembly were recorded by Zeta sizer Nano-ZS dynamic light scattering (DLS, Malvern Instruments, UK). Slight light scattering (SLS) was measured on DAWN HELEOS-Ⅱ multi-angle light scattering detector to determine Rg. TEM was performed

on H-600 (Hitachi, Japan) with the acceleration voltage of 75 kv. The conductivity measurements were completed by Zeta sizer Nano-ZS dynamic light scattering to determine critical assembly concentration (CAC). Each self-assembly was prepared with the certain concentration gradient and plotted curve according to the conductivity at different concentration.

2. Synthesis of Fc-(CD-N_3)$_2$



Scheme S1 Synthetic routes of Fc-(CD-N_3)$_2$.

2.1 Bis (2-azidoethyl) amine (EA-(N_3)$_2$) was synthesized according to the literature.[1]

2.2 Synthesis of bis(2-azidoethyl) amine Ferrocene [Fc-(N_3)$_2$]

Ferrocene carboxylic acid (2.30 g, 10 mmol) and DMAP (0.37 g, 3 mmol) were dissolved in 50 mL dry THF. The solution was ice bath for 30 minutes to activate carboxyl. Then EA-(N_3)$_2$ (1.87 g, 12 mmol) was added by slowly dropping at 0 ^{o}C. After ice bath for another 20 min, EDC·HCl (2.30 g, 12 mmol) was added as the dehydrating agents and catalysts. The solution was allowed to react at room temperature for 24 h. After the reaction, removed the precipitation by suction filtration and collected the filtrate. Then the filtrate was rotary evaporation and the product was dissolved in chloroform again and washed with saturated sodium chloride solution for three times. The crude product was further purified by silica gel column chromatography using n-hexane/ethyl acetate (2:1 v/v) as the eluent. After removing the solvent by a rotary evaporator, the red viscous liquid was obtained as the final product (2.36 g, yield: 64.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm)= [4.66 (s, 2H), 4.36 (s, 2H), 4.25 (s, 5H), protons in ferrocene], 3.69 (s, 4H, -CH_2-C**H**$_2$-N_3), 3.57 (s, 4H, -C**H**$_2$-CH_2-N_3).

^{13}C NMR (100 MHz, $CDCl_3$): δc (ppm)= 171.5 (-**C**O$N(CH_2CH_2N_3)$), [77.59, 70.55, 69.92, carbons in ferrocene], 49.78 (-CO$N(\mathbf{C}H_2CH_2N_3)_2$), 47.92 (-CO$N(CH_2\mathbf{C}H_2N_3)_2$).

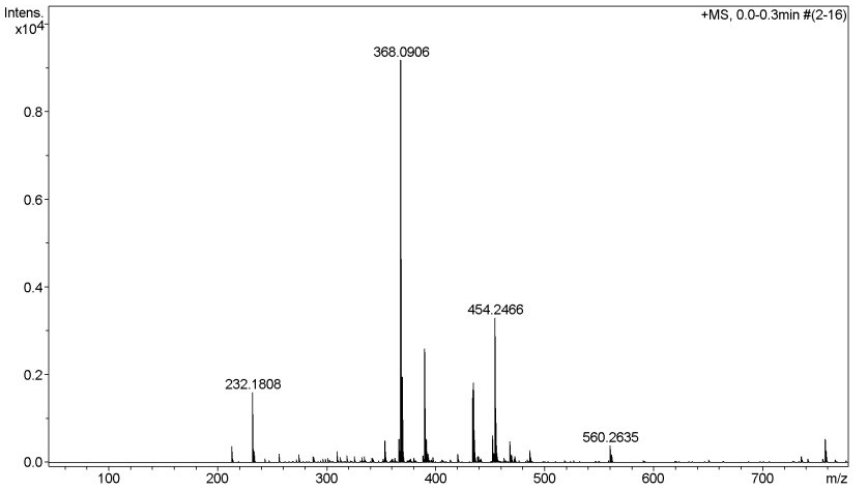


Fig. S1 Electrospray ionization mass spectrometry (EI-MS) of Fc-$(N_3)_2$, [CH_3OH, m/z]: calcd for $C_{15}H_{17}FeON_7$: 367.08, found for $[M+H]^+$: 368.0906.

2.3 Synthesis of Mono-6-deoxy-6-(p-tolylsulfonyl)-β-CD-≡ (≡-β-CD-OTs)

Mono-6-deoxy-6-(p-tolylsulfonyl)-β-CD and mono-6-deoxy-6-alkyne β-CD (β-CD-≡) monomers were synthesized according to the previous literatures. β-CD-≡ (6.22 g, 5.3 mmol) was dissolved in 100 mL, 0.4 M NaOH aqueous solution. The flask was cooled to 0 °C in the ice bath. TsCl (1.01 g, 5.3 mmol) was slowly added about 30 min. After 4 h of stirring the mixture at 0 °C, the precipitate was removed by suction filtration. Then the pH value of the filtrate was adjusted to 8 by dropping hydrochloric acid solution. Then the mixture was stored at 0 °C overnight with the white solid precipitation gradually. The resulting white precipitate was collected by suction filtration and washed by acetone/deionized water (8:1 v/v) for three times. The final product was dried in a vacuum oven at 40 °C, yielding a white solid (1.69g, yield: 24.1%). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm)= [7.75 (d, 2H), 7.43 (d, 2H), 2.43 (s, 3H), proton inp-toluene sulfonyl], 5.74 (s, 14H, **2, 3-OH**), 4.84 (s, 7H, **1-H**), 4.53 (s, 5H, **6-OH**), 3.50-3.85 (s, 28H, **3, 5, 6-H**), 3.13-3.44 (s, 14H **2, 4-H**), 2.79 (d, 2H -C≡C**H**). ^{13}C NMR (100 MHz, DMSO-d_6): δc (ppm)= [145.62, 133.47, 130.40, 128.21, 21.62, carbons in p-toluene sulfonyl)], 102.81 (**C**-1), 83.76(-NHCH2**C**≡CH), 82.38(**C**-4), 74.17-72.19 (**C**-2, 3, 5), 71.14(-NHCH2C≡**C**H), [70.20, 69.40 (**C**-6')], 60.82(**C**-6), 38.17(-NH**C**H2C≡CH).

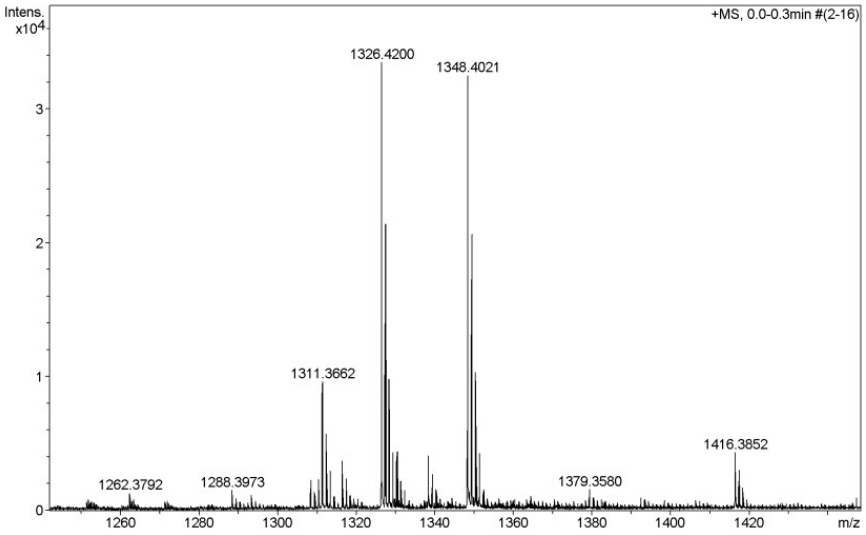


Fig. S2 Electrospray ionization mass spectrometry (EI-MS) of ≡-β-CD-OTs, [CH_3OH, m/z]: calcd for $C_{52}H_{79}O_{36}NS$: 1325.41, found for $[M+H]^+$: 1326.4200, $[M+Na]^+$: 1348.4021.

2.4 Synthesis of Fc-(CD-OTs)$_2$

The typical azide-alkyne click reaction was used in this step. Fc-$(N_3)_2$ (73.4 mg, 0.2 mmol), ≡-β-CD-OTs (636.2 mg, 0.48 mmol) and PMDETA (42 μL, 0.2 mmol) were dissolved in 5 mL DMF. Then the mixture was subjected one brief freeze-vacuum-thaw cycle in order to remove oxygen. Next, CuBr (28.8 mg, 0.2 mmol) was added in solution with nitrogen atmosphere and the shrek tube was carefully removed oxygen by three freeze-vacuum-thaw cycles. Then the mixture was stirred in an oil bath at 65 °C for 48 h. After the reaction, exposing the mixture to the air to stop the reaction. When the mixture solution was cooled to room temperature, precipitated into an excess of cold acetone three times to obtain the yellow solid. Next, the crude product was dissolved in 5 mL DMF, and the mixture was dialyzed (molecular weight cut off: 1000) in deionized water for 1 d to remove the excess β-CD-OTs-≡. After removing of the water by freeze drying, a yellow powder was obtained (304.1 mg, yield: 50.4%). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm)= 7.92 (s, 2H, **triazole ring**), 5.71 (s, 28H, **2, 3-OH**), 4.83 (s, 14H, **1-H**), 4.54 (s, 10H, **6-OH**), [4.37 (s, 2H), 4.31 (s, 2H), 4.18 (s, 5H), proton in **Ferrocene**], 3.50-3.89 (s, 28H, **3, 5, 6-H**), 3.21-3.45 (s, 14H **2, 4-H**), 2.81 (d, 2H -C≡C**H**). ^{13}C NMR (100 MHz, DMSO-d_6): δc (ppm)= 170.57 (-**C**ON(CH2CH2-)), [146.99, 123.51 (carbons in **Triazole**)], [145.32, 133.11, 130.37, 128.06, 21.68, carbons in p-toluene sulfonyl)], 102.48 (**C-1**), 83.67 (-NHCH2**C**≡CH), 81.98(**C-4**), 73.77-72.25 (**C-2, 3, 5**), 71.39 (-NHCH2C≡**C**H), 70.50-69.90 (carbons in **Ferrocene**), [69.81, 69.37 (**C-6'**)], 60.38(**C-6**), 38.36(-NH**C**H2C≡CH).

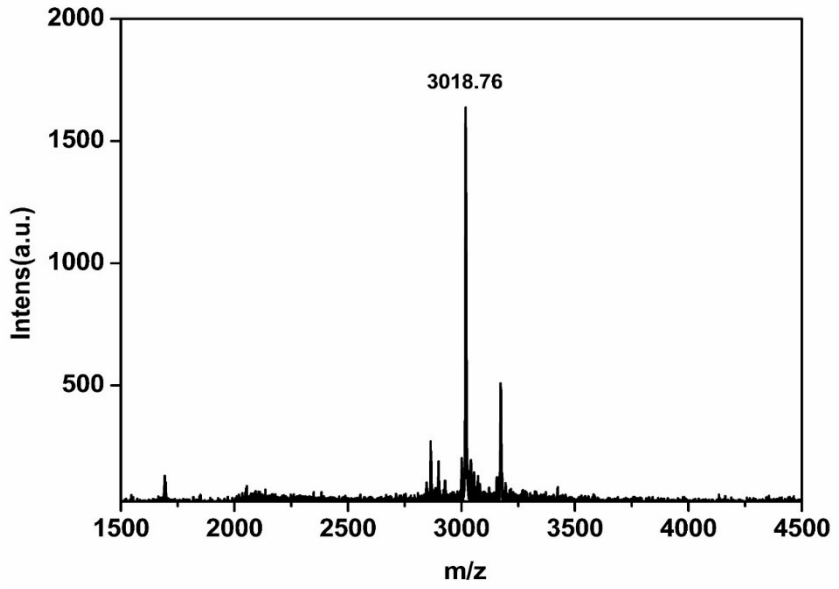


Fig. S3 MALDI-TOF-MS of Fc-(CD-OTs)$_2$ [CH_3OH, m/z]: calcd for $C_{119}H_{175}O_{73}N_9S_2Fe$: 3017.90, found for $[M+H]^+$: 3018.76.

2.5 Synthesis of Fc-(CD-N_3)$_2$

Fc-(CD-OTs)$_2$ (301.7 mg, 0.1 mmol), NaN_3 (65 mg, 1.0 mmol) were dissolved in 5 mL dried DMF. Then introducing the nitrogen into the solution to remove the oxygen. Then the mixture solution was stirred in an oil bath at 80 °C for 12 h. After the reaction, cooling the flask to make the system reduce at room temperature, then precipitated into an excess of cold acetone twice to obtain the yellow solid. Next, the crude product was dissolved in 5 mL DMF/deionized water (2:3 v/v), and the mixture was dialyzed (molecular weight cut off: 500) for 1 d to remove the excess NaN_3. After removing of the water by freeze drying, a yellow powder was obtained (224.7 mg, yield: 81.4%). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm)= 7.92 (s, 2H, protons in **triazole ring**), [7.75 (d, 4H), 7.43 (d, 4H), 2.43 (s, 6H), proton in tolylsulfonyl], 5.75 (s, 28H, **2, 3-OH**), 4.81 (s, 14H, **1-H**), 4.54 (s, 10H, **6-OH**), [4.37 (s, 2H), 4.30 (s, 2H), 4.17 (s, 5H), proton in **Ferrocene**], 3.52-3.85 (s, 28H, **3, 5, 6-H**), 3.17-3.46 (s, 14H **2, 4-H**), 2.70 (d, 2H -C≡C**H**). ^{13}C NMR (100 MHz, DMSO): δc (ppm)= 170.47 (-**C**ON(CH2CH2-)), [147.01, 123.55 (Carbons in **Triazole**)], 102.25 (**C-1**), 83.56 (-NHCH2**C**≡CH), 82.00(**C-4**), 74.25-72.22 (**C-2, 3, 5**), 70.66 (-NHCH2C≡**C**H), 70.34-69.74 (carbons in **Ferrocene)**, 60.12(**C-6**), 36.33(-NH**C**H2C≡CH).

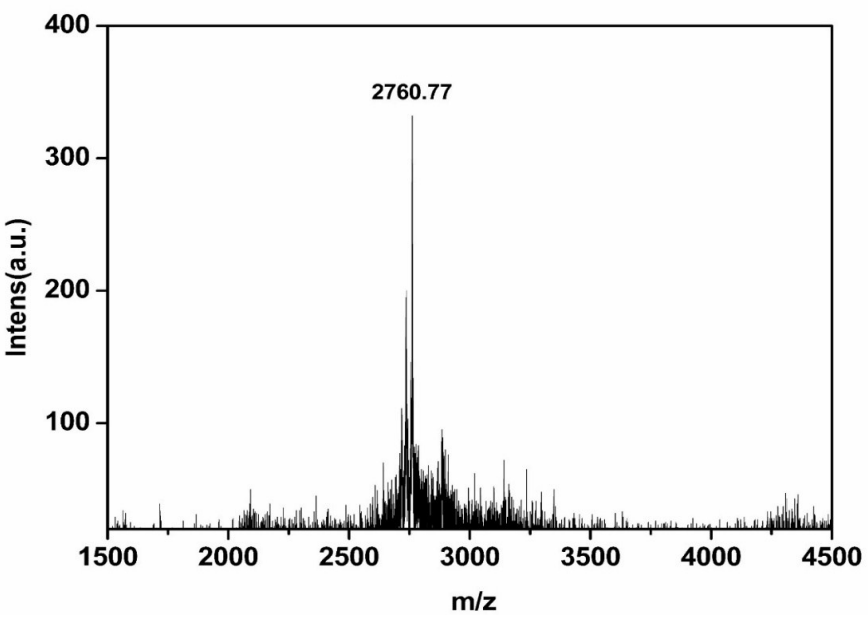


Fig. S4 MALDI-TOF-MS of Fc-$(N_3)_2$ [CH_3OH, m/z]: calcd for $C_{105}H_{161}O_{67}N_{15}Fe$: 2759.90, found for $[M+H]^+$: 2760.77.

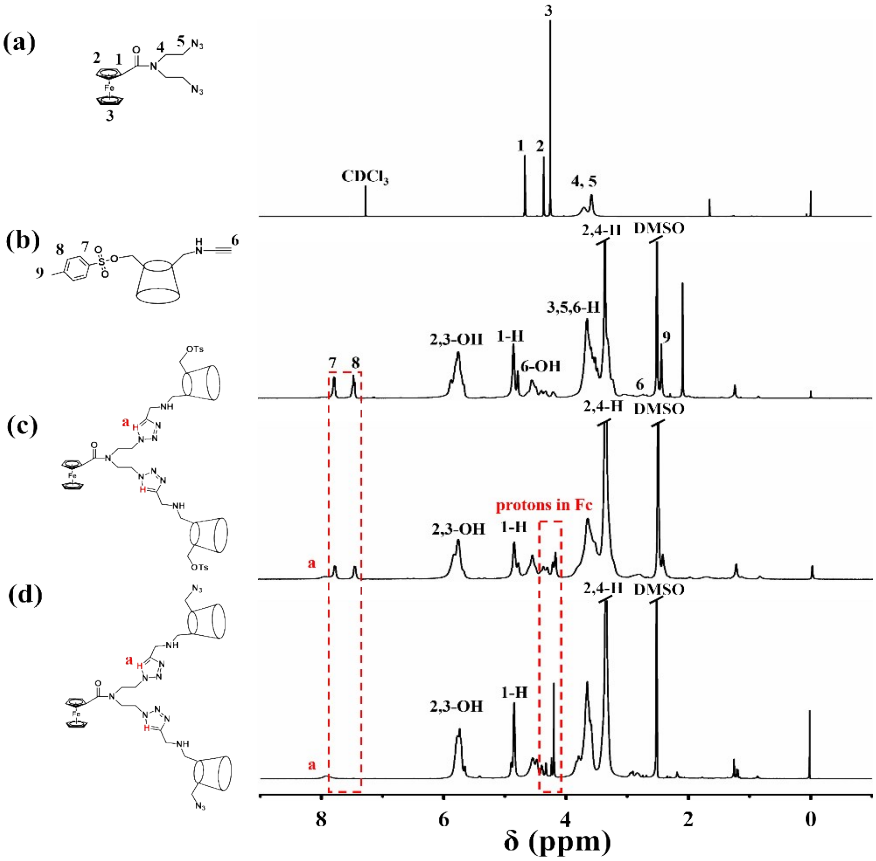


Fig. S5 ^{1}H-NMR spectra of (a) Fc-$(N_3)_2$, (b) ≡-β-CD-OTs, (c) Fc-$(CD\text{-}OTs)_2$, and (d) Fc-$(CD\text{-}N_3)_2$.

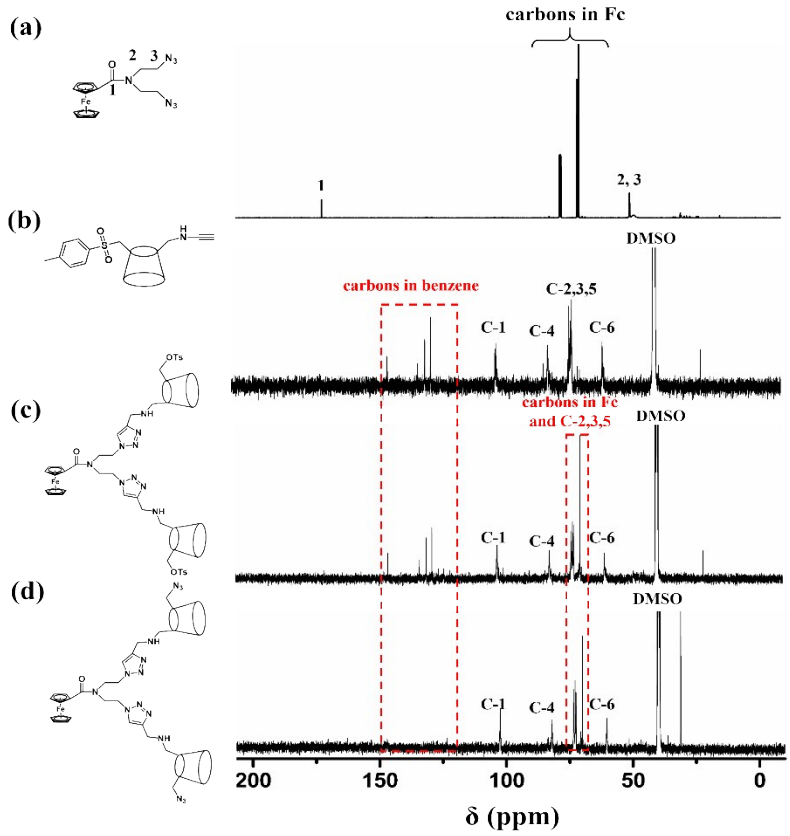
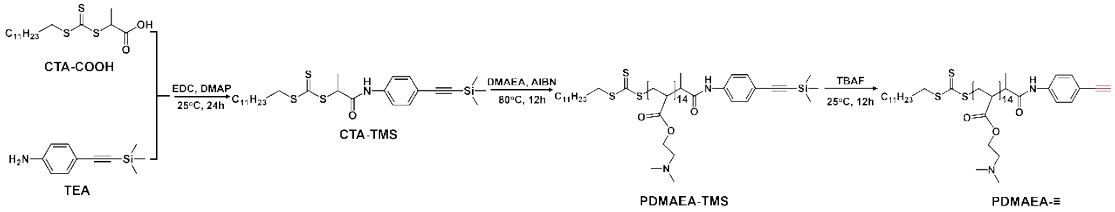


Fig. S6 ^{13}C-NMR spectra of (a) Fc-$(N_3)_2$, (b) ≡-β-CD-OTs, (c) Fc-$(CD\text{-}OTs)_2$, and (d) Fc-$(CD\text{-}N_3)_2$.

3. Synthesis of PDMAEA-≡



Scheme S2 Synthetic routes of PDMAEA-≡

3.1 Synthesis of 2-{[(dodecylsulfanyl)carbonothioyl]sulfanyl}propanoic acid(CTA-COOH)

Sodium hydroxide(0.50 g) and tetrabutylammonium bromide (64.4 mg, 0.2 mmol) were dissolved in a mixture of water(5 mL), acetone(40 mL), and 1-dodecanethiol (2.5 g, 12.5 mmol) with stirring at room temperature. Next, the mixture was placed into an ice bath and adding CS_2(0.95 g, 12.5 mmol) at 0 °C. Then, the flask was ice bath for 20 minutes and slowly adding bromopropionic acid (1.91 g, 12.5 mmol) into mixture. Finally, putting the flask into the oil bath and reacted for 12 hours at 30 °C.

When the reaction was over, removed acetone by rotary evaporation, then diluted with 50 mL

hydrochloric acid and 150 mL water. After stirring for 10min, the yellow solid precipitate was collected by suction filtration. Finally, the product was recrystallized twice in n-hexane for purification (3.68 g, yield: 84.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm)= 4.86 (q, 1H, -C**H**(CH_3)-COO-), 3.36 (t, 2H, -CH_2-CH_2-C**H$_2$**-S-), 1.70 (m, 2H, -CH_2-C**H$_2$**-CH_2-S-), 1.62 (d, 3H, -CH(C**H$_3$**)-COO-), 1.39 (m, 2H, -CH_2-CH_2-C**H$_2$**-S-), 1.34 – 1.20 (s, 16H, CH_3-(C**H$_2$**)$_8$-), 0.89 (t, 3H, C**H$_3$**-$(CH_2)_8$-).

3.2 Synthesis of 4-[2-(Trimethylsilyl)ethynyl] aniline(TEA)

Ethynyltrimethylsilane (0.99 mL, 7 mmol), 4-iodoaniline (1.10 g, 5 mmol), and bis(triphenylphosphine)palladium(II) chloride (70.2 mg, 0.1 mmol) were dissolved in THF and moved to shrek tube, then the mixture was subjected one brief freeze-vacuum-thaw cycles in order to remove oxygen. Next, CuI (19.1 mg, 0.1 mmol) was added in solution with nitrogen atmosphere and the shrek tube was carefully removed oxygen by three freeze-vacuum-thaw cycles. Finally, the mixture was stirring at room temperature for 12 hours. After the reaction, removed the precipitation by suction filtration and collected the filtrate. The filtrate was rotary evaporation and the solid was dissolved in chloroform again to purify by extraction wash with saturated sodium chloride solution. The crude product was further purified by silica gel column chromatography using petroleum ether/ethyl acetate (4:1 v/v) as the eluent. After removing the solvent by rotary evaporator, the light brown solid was obtained as the final product (0.73 g, yield: 77.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = [7.28 (d, 2H), 6.58 (d, 2H), proton in benzene], 3.79 (s, 2H, N**H$_2$**-benzene-), 0.23 (s, 9H, -Si(C**H$_3$**)$_3$).

3.3 Synthesis of 3-(Trimethylsilyl)prop-2-{[(dodecylsulfanyl)carbonothioyl]sulfanyl}propanoic acid propanoate alkyne-functionalized RAFT agent(CTA-TMS)

2-[[(Dodecylthio)thioxomethyl]thio]propanoic acid (350.6 mg, 1.0 mmol) and DMAP(122.2 mg, 1.0 mmol) dissolved in 15 mL dry dichloromethane. The solution was ice bath for 20 minutes to activate carboxyl. Then the 4-[2-(Trimethylsilyl)ethynyl]aniline (227.1 mg, 1.2 mmol) was added by slowly dropping at 0 ^{o}C. After ice bath for another 20min, EDC·HCl (230.1 mg, 1.2 mmol) was added as the dehydrating agents and catalysts. The solution was allowed to react at room temperature for 24 h. After the reaction, the mixture was purification by extraction wash with

saturated sodium chloride solution. the crude product was further purified by silica gel column chromatography using petroleum ether/ethyl acetate (6:1 v/v) as the eluent. After removing the solvent by a rotary evaporator, the bright yellow solid was obtained as the final product (373.3 mg, yield: 71.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm)= 8.53 (s, -N**H**CO-), 7.41 (q, 4H in benzene), 4.91 (s, 1H, -C**H**(CH_3)-COO-), 3.39 (t, 2H, -C**H$_2$**-CH_2-CH_2-S-), 1.72 (m, 2H, -CH2-C**H$_2$**-CH2-S-), 1.62 (d, 3H, -CH(C**H$_3$**)-COO-), 1.42 (m, 2H, -CH_2-CH_2-C**H$_2$**-S-), 1.28 (s, 16H, CH_3-(C**H$_2$**)$_8$-), 0.90 (t, 3H, C**H$_3$**-(CH_2)8-), 0.25 (s, 9H,-Si(C**H$_3$**)$_3$).

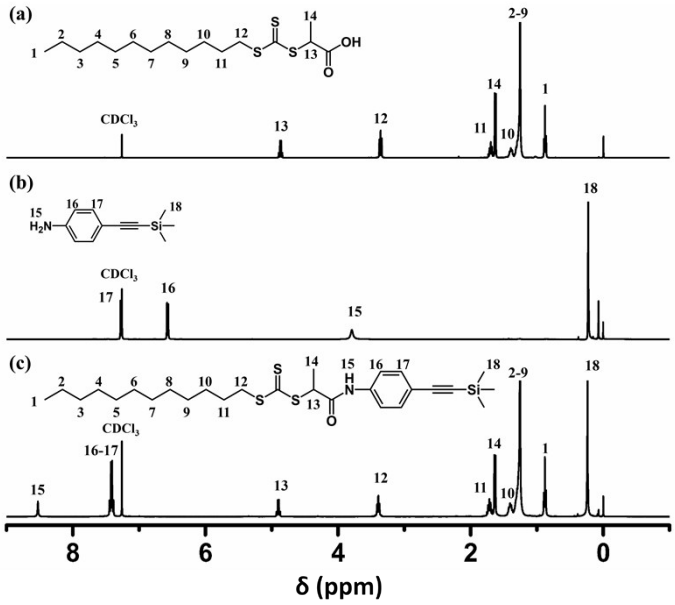


Fig. S7 ^{1}H-NMR spectra of (a) CTA-COOH, (b) TEA and (c) CTA-TMS.

3.4 Synthesis of PDMAEA-TMS

PDMAEA-TMS was synthesized by reversible fracture-addition polymerization (RAFT). CTA-TMS (52.2 mg, 0.1 mmol), DMAEA (200.4 mg, 1.4 mmol), AIBN (4.1 mg, 0.25 mmol) were dissolved in 5 mL dried 1,4-dioxane. When the reactants were fully dissolved, the reaction tube was carefully subjected to three freeze-pump-thaw cycles to remove oxygen. And then mixture was stirred at 70 ^{o}C for 12 h. After the reaction, precipitated into an excess of cold n-hexane three times to remove unreacted reactant. Finally, the product was dried in a vacuum oven at 40 °C overnight, yielding the light yellow viscous liquid (186.4 mg, yield: 78.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm)=7.40 (4H, proton form benzene in RAFT agent), 4.14 (28H, -COO-C**H$_2$**-CH_2-, proton in*DMAEA*), 2.55 (28H, -COO-CH_2-C**H$_2$**-, proton in *DMAEA*), 2.26 (91H, -CH_2-CH_2-N(C**H$_3$**)$_2$, proton in *DMAEA*), 0.23 (s, 9H, -C≡C-Si(C**H$_3$**)$_3$ in RAFT agent). ^{13}C NMR (100 MHz,

$CDCl_3$): δc (ppm)= 174.36 (-**C**OO-CH_2-CH_2- in DMAEA), 172.83 (-CH(CH_3)-**C**OO- in RAFT agent), 132.60-120.89 (carbons form **benzene** in RAFT agent), 105.08-93.54 (carbons form -**C**≡**C**-Si(CH_3)$_3$ in RAFT agent), 62.34(-COO-**C**H_2-CH_2- in DMAEA), 57.46(-COO-CH_2-**C**H_2- in DMAEA), 45.71(-CH_2-CH_2-N(**C**H_3)$_2$ in DMAEA), 41.21-14.13 (carbons form alkyl in main chain). $M_{n,GPC}$=1500, $M_{w,GPC}$=1800, M_w/M_n=1.20.

3.5 Synthesis of PDMAEA-≡

Protected Dodecyl-PDMAEA-TMS (300 mg, 0.1 mmol) was dissolved in 10 mL dried THF and the flask was purged with nitrogen for 15 minutes. When the solution was cooled to -20 °C, 30 μL acetic acid was added into the mixture. Then TBAF in THF (200 μL, 1 M) was added dropwise into the reaction mixture. After that, stirring for 30 minutes at -20 °C, followed by stirring at room temperature for another 12 h. After the reaction, removing the solvent by a rotary evaporator, then dissolved the product in 3 mL dried dichloromethane, and precipitated into an excess of cold n-hexane five times to remove impurities. Then the crude product was further purified by dialysis (molecular weight cut off: 500). The finally product was obtained by freeze drying (224.7 mg, yield: 77.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm)=7.41 (4H, proton form benzene in RAFT agent), 4.20 (27H, -COO-C**H**$_2$-CH_2-, proton in *DMAEA*), 2.70 (28H, -COO-CH_2-C**H**$_2$-, proton in *DMAEA*), 2.36 (90H, -CH_2-CH_2-N(C**H**$_3$)$_2$, proton in *DMAEA*).

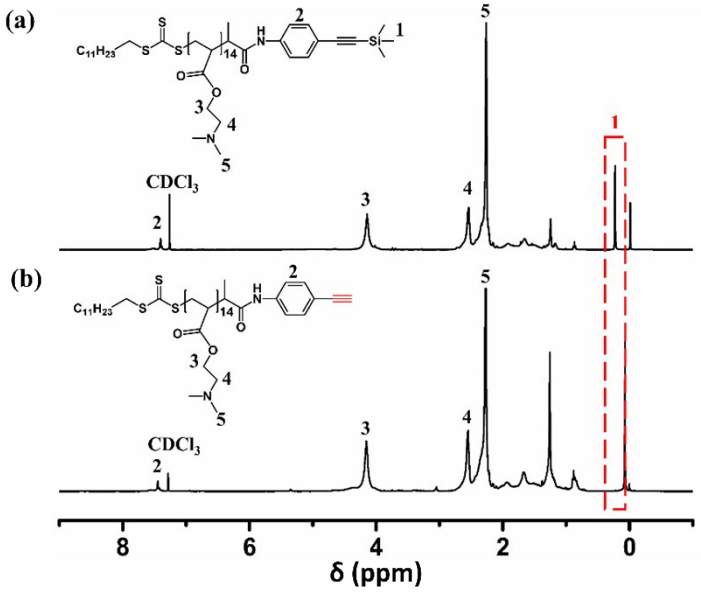


Fig. S8 ^{1}H-NMR spectra of (a) PDMAEA-TMS and (b) PDMAEA-≡.

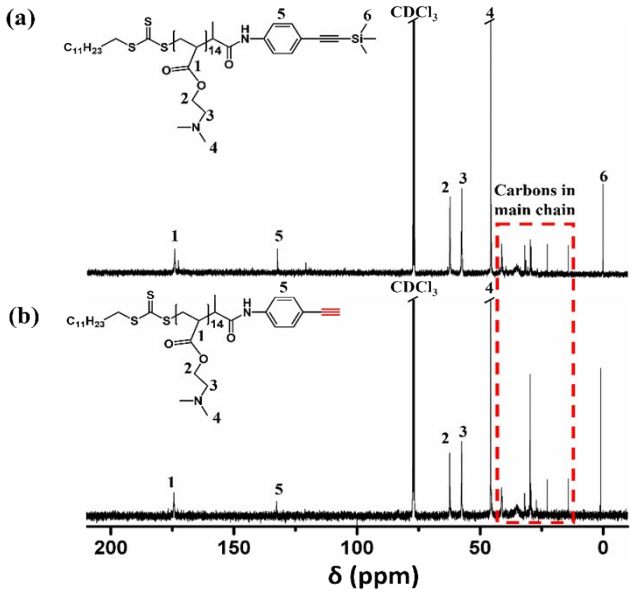
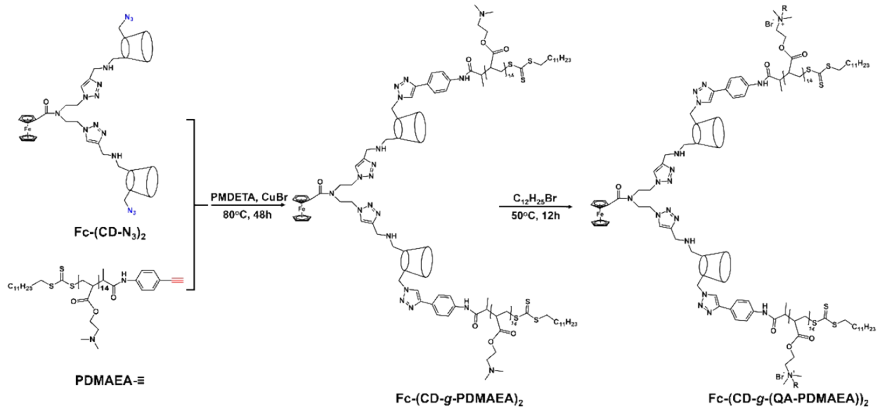


Fig. S9 ^{13}C-NMR spectra of (a) PDMAEA-TMS and (b) PDMAEA-≡.

4. Synthesis of Fc-(CD-*g*-(QA-PDMAEA))$_2$



Scheme S3 Synthetic routes of Fc-(CD-*g*-(QA-PDMAEA))$_2$.

4.1 Synthesis of Fc-(CD-*g*-PDMAEA)$_2$

The typical azide-alkyne click reaction was used in this step. PDMAEA-≡ (300 mg, 0.1 mmol), Fc-(CD-N_3)$_2$ (82.8 mg, 0.03 mmol) and PMDETA (10 μL, 0.05 mmol) were dissolved in 5 mL DMF. Then the mixture was subjected one brief freeze-vacuum-thaw cycles in order to remove oxygen. Next, CuBr (7.2 mg, 0.05 mmol) was added in solution with nitrogen atmosphere and the shrek tube was carefully removed oxygen by three freeze-vacuum-thaw cycles. After being stirred in oil bath at 80 °C for 24 h, precipitated into an excess of cold ethyl ether/n-hexane (3:1 v/v) twice to obtain the solid. Next, the crude product was dissolved in 5 mL DMF, and the mixture was dialyzed (molecular weight cut off: 1000) in deionized water for 2 d to remove the excess unreacted reactant and CuBr. After removing of the water by freeze drying, a yellow powder was

obtained (142.1mg, yield: 60.7%). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm)= [8.40, 7.99 (4H, protons in *triazole ring*)], 7.69 (8H, proton form *benzene* in RAFT agent), 5.81 (28H, **2, 3-OH**), 4.85 (14H, **1-H**), 4.54 (10H, **6-OH**), [4.41-4.15, proton in *Ferrocene*], 4.09 (59H, -COO-C**H**$_2$-CH_2-, proton in *DMAEA*), 2.18 (171H, -CH_2-CH_2-N(C**H**$_3$)$_2$, proton in *DMAEA*). $M_{n,GPC}$ =5500, $M_{w,GPC}$ =7200, M_w/M_n=1.30.

4.2 Synthesis of Fc-(CD-*g*-(QA-PDMAEA))$_2$

Fc-(CD-*g*-PDMAEA)$_2$ (90 mg, 0.01 mmol) and excess 1-bromododecane (74.8 mg, 0.3 mmol) were dissolved in 5 mL DMF. Then the flask was purged with nitrogen for 15 minutes. Next, the mixture was stirred in an oil bath at 70 °C for reaction. After stirring 24 h, precipitated into an excess of cold ethyl ether three times to remove unreacted 1-bromododecane. Finally, the crude product was dissolve in 5 mL DMF and dialyzed (molecular weight cut off: 3000) against deionized water for 48h to purify the product. The products were freeze dried to obtain quaternized products (yellow solid, 101.5 mg, yield: 67.7%). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm)= [8.36, 7.96 (4H, proton in *Triazole ring*)], 7.76 (8H, proton form benzene in RAFT agent), 5.84 (28H, **2, 3-OH**), 4.85 (14H, **1-H**), 4.73-4.28 (protons in **6-OH** and -COO-C**H**$_2$-CH_2- in *QA-PDMAEA*), 4.36-3.99 (protons in *Ferrocene*), 3.94-3.00 [protons in **2, 3, 4, 5, 6-H** and -N^+(C**H**$_3$)$_2$- from *QA-PDMAEA*],1.25[protons form –CH_2-(C**H**$_2$)$_9$-CH_3 in dodecyl], 0.86[protons form –CH_2-(CH_2)$_9$-C**H**$_3$ in dodecyl].

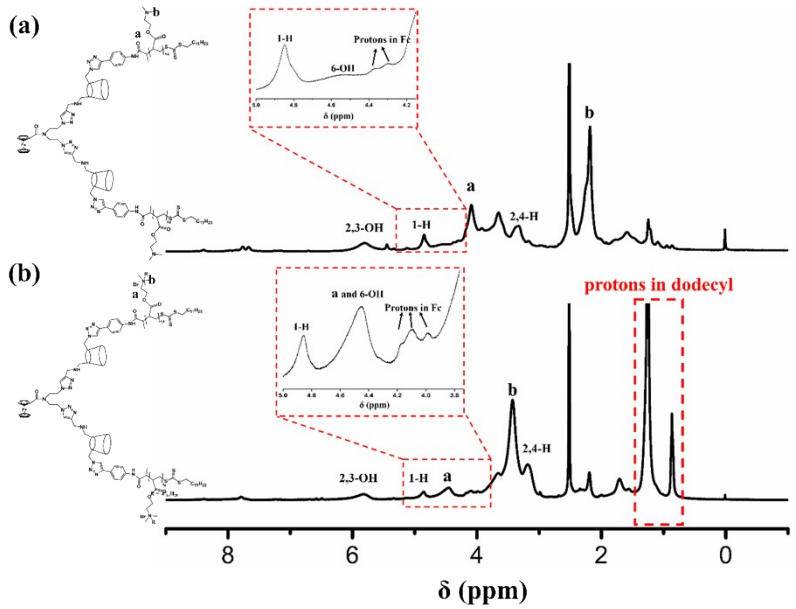


Fig. S10 ^{1}H-NMR spectra of (a) Fc-(CD-*g*-PDMAEA)$_2$ and (b) Fc-(CD-*g*-(QA-PDMAEA))$_2$.

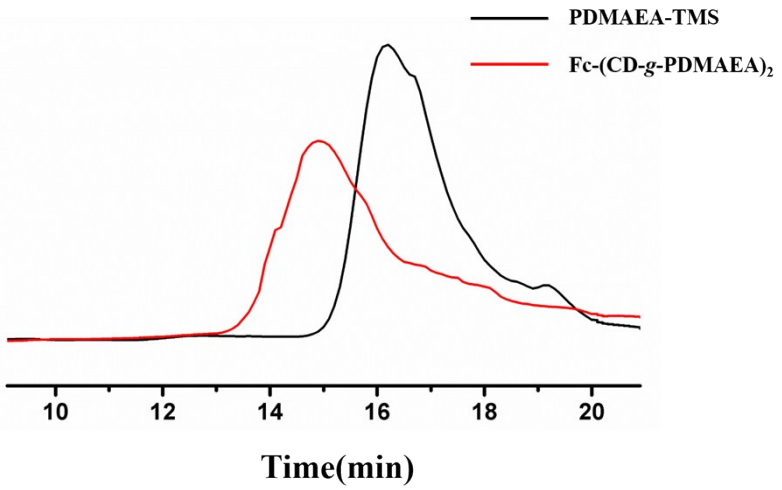


Fig. S11 GPC spectra of PDMAEA-TMS (blank line) and Fc-(CD-*g*-PDMAEA)$_2$ (red line).

5. Self-assembly behaviors of Fc-(CD-*g*-(QA-PDMAEA))$_2$

5.1 Self-assembly behavior of the dot-like assemblies after adding excess GSH

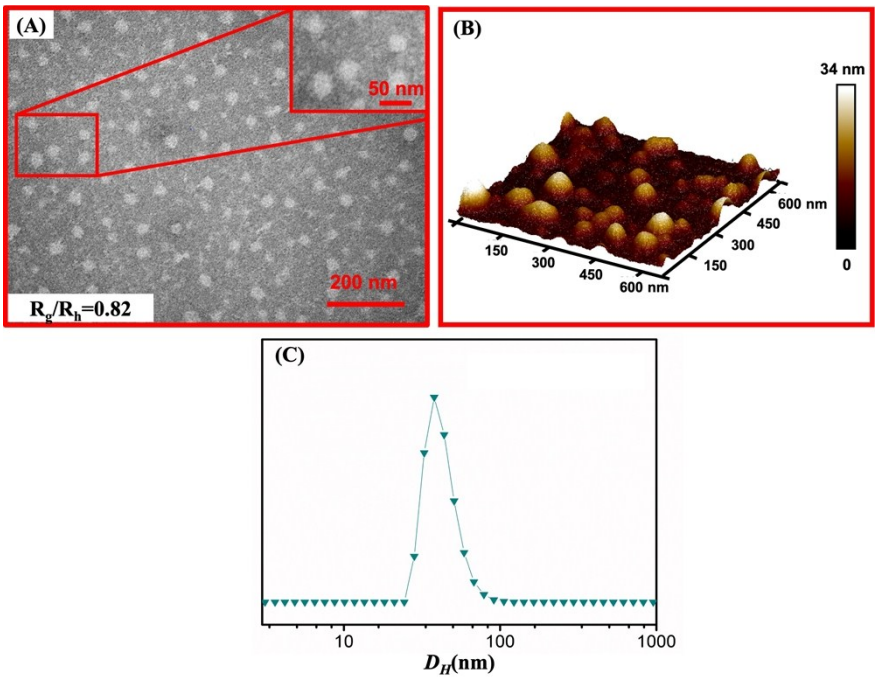


Fig. S12 (A) Typical TEM image, (B) AFM image, and (C) DLS curve of dot-like assemblies after adding excess GSH.

5.2 I_1/I_3 values of pyrene solution under different conditions

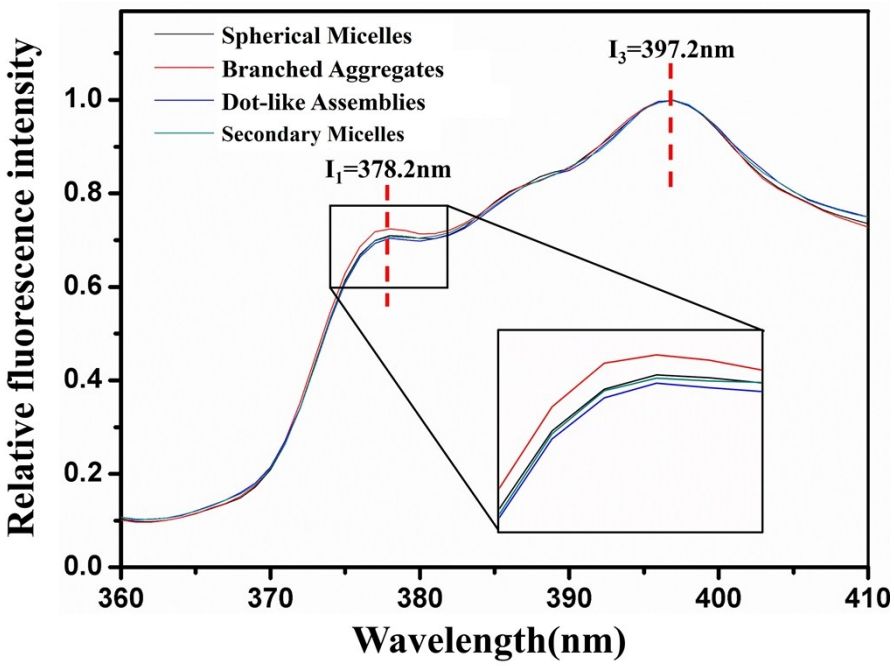


Fig. S13 I_1/I_3 values of pyrene to determine hydrophobic micro-domains. Setting the value of I_3 to 1 to observe the change in relative fluorescence intensity of I_1.

Table S1 I_1/I_3 values of pyrene solution under different conditions.

Sample	I_1/I_3 values[a]
Pyrene solution	1.025±0.001
Spherical Micelles	0.712±0.003
Branched Aggregates	0.722±0.002
Dot-like Assemblies	0.704±0.003
Secondary Micelles	0.717±0.004

[a]**The measure mothed to detemine I_1/I_3 value of pyrene were detailed described in the section of Experimental Section.**

5.3 Critical aggregation concentration (CAC) test

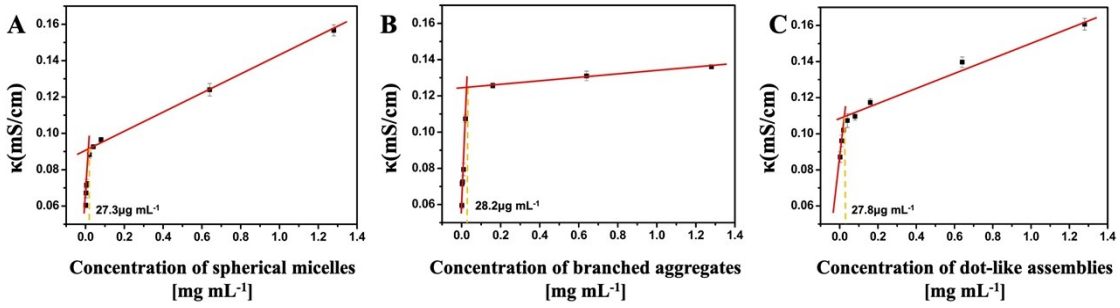


Fig. S14 CAC detection plots determining by conductance versus various concentration of self-assemblies: (A) spherical micelles, (B) branched aggregates, (C) dot-like assemblies.

6. Biological properties of self-assemblies

6.1 MIC, MBC test

In this experiments, the Gram-negative bacteria (*E. coli*) and Gram-positive bacteria (*S. aurens*) were chosen for test. First, 100 μL LB medium containing bacteria with the same concentration (2×10^5 cfu mL^{-1}) was dispensed to the wells of 96-well plates. Then another 100 μL LB medium containing each assembly was added into the aforementioned solution to achieve a final concentration of 0, 1, 2, 4, 8 ,16, 32, 64, 128, 256, 512, 1024 μg mL^{-1}. The 96-well plates were incubated at 37 °C, and observed the growth of bacteria after 12 h. Similarly, the MIC value was defined as the lowest concentration of the antibacterial agents that no visible growth of bacteria was observed (the culture are not cloudy). As for the MBC test, 10μL of the bacterial culture after MIC tests (diluted to 100 μL) was spread on the solid LB agar-plate, and observed the growth of colonies after incubation at 37 °C for 12 h. The MBC values was defined as the lowest concentration of the antibacterial agents that no plaque of bacterial colonies were observed after incubation for 12 h.

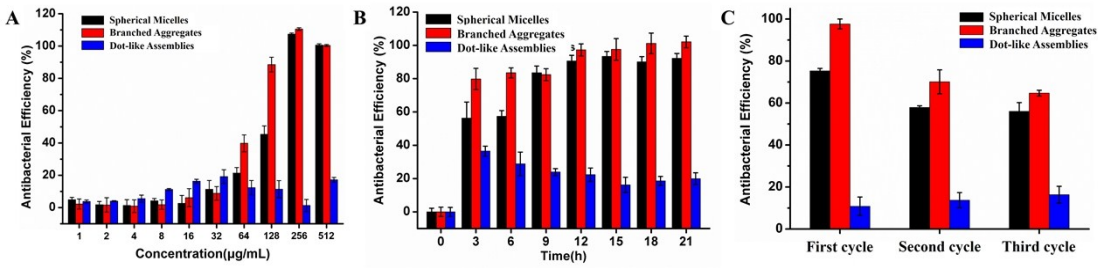


Fig. S15 Antibacterial activities of Fc-(CD-*g*-(QA-PDMAEA))$_2$ self-assemblies toward *S. aureus* group. (A) The relationship between antibacterial efficiency and concentration among three self-assemblies. (B) The relationship between antibacterial efficiency and time of three self-assemblies. (C) Antibacterial activity change tendency under periodic cycles. [Fc-(CD-*g*-(QA-PDMAEA))$_2$]=128 μg mL^{-1}.

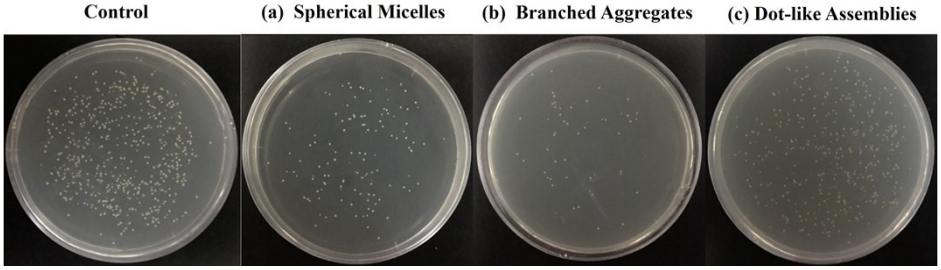


Fig. S16 Colony forming units (CFU) for *S. aureus* treated with three self-assemblies on LB agar plate, treated with (a) spherical micelles, (b) branched aggregates, (c) dot-like assemblies. [Fc-(CD-*g*-(QA-PDMAEA))$_2$]=128 μg mL^{-1}.

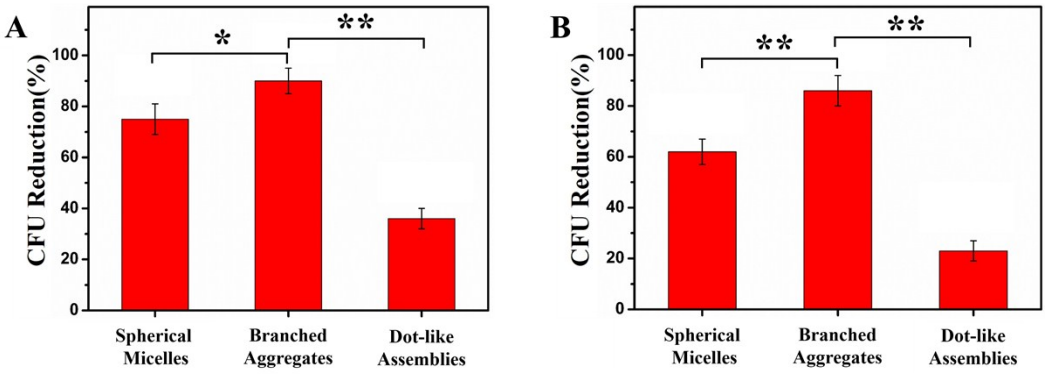


Fig. S17 Antibacterial activity among three assemblies calculated by colony forming units. (A) *E. coli* and (B) *S. aureus*. *$p < 0.05$, **$p < 0.01$. [Fc-(CD-*g*-(QA-PDMAEA))$_2$]=128 μg mL^{-1}.

6.2 Cell apoptosis study by live/dead cell staining

Three types of assemblies were respectively added to 200 μL of PBS buffer (containing 1×10^8 cfu mL^{-1}) for 2 hours, and rinsed three times by PBS. Then, all samples were soaked into 20 μL staining solution containing Hoechst 33258(25 μM) and propidium iodide (30 μM) for live/dead staining. After incubation 15 min, using confocal microscopy (an oil immersed 63×objective lens) to observe the stained bacteria. The excitation wavelength of Hoechst 33258 was 405 nm and the excitation wavelength of propidium iodide was 535 nm.

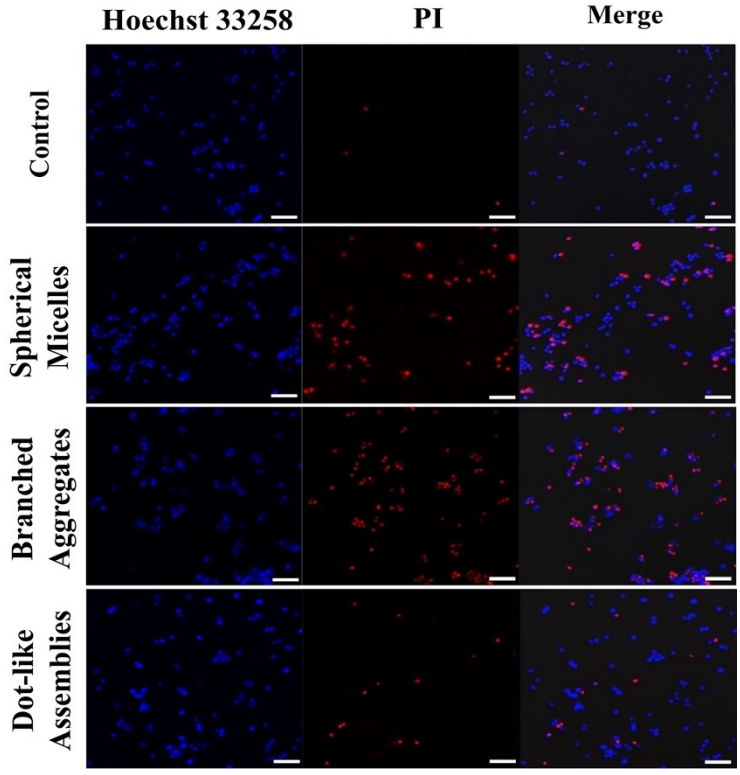


Fig. S18 CLSM images of antibacterial activities about *S. aureus* using live/dead bacterial viability assay. [Fc-(CD-*g*-(QA-PDMAEA))$_2$]=128 μg mL^{-1}. Scale bars: 10μm.

6.3 In Vitro Hemolysis Assay for biocompatibility test

The hemolytic activities of various assemblies were determined by Human Red Blood Cells (RBCs). Fresh RBCs were separated from 2 mL of citrated blood by centrifugation. The cells were washed thrice by PBS (pH 7.4) in order to remove plasma and then resuspended RBCs into 10 mL of PBS. 100μL of diluted RBCs suspension was treated with equal volume of each assembly at gradient concentrations and incubated at 25 °C for 30 min. After incubation, the mixture was centrifuged at 1000 g for 5 min and the absorbance of the supernatant was measured at 540 nm using microplate reader. RBCs treated with Triton X-100 (2%) and PBS was used as the positive and negative controls, respectively. The percentages of hemolysis of RBCs was calculated using the formula:

$$\text{Hemolysis}(\%) = (OD^{sample} - OD^{negative})/(OD^{positive} - OD^{negative}) \times 100$$

6.4 Zeta potential measurements

E. coli and *S. aurens* were centrifuged and resuspended in PBS containing three specific morphology assemblies separately. Then the mixed samples were incubated for 30 min at 25 °C. Then, the bacteria were obtained by centrifuging and the precipitates were suspended into pure water for zeta potential measurements. All samples were taken with three replicates.

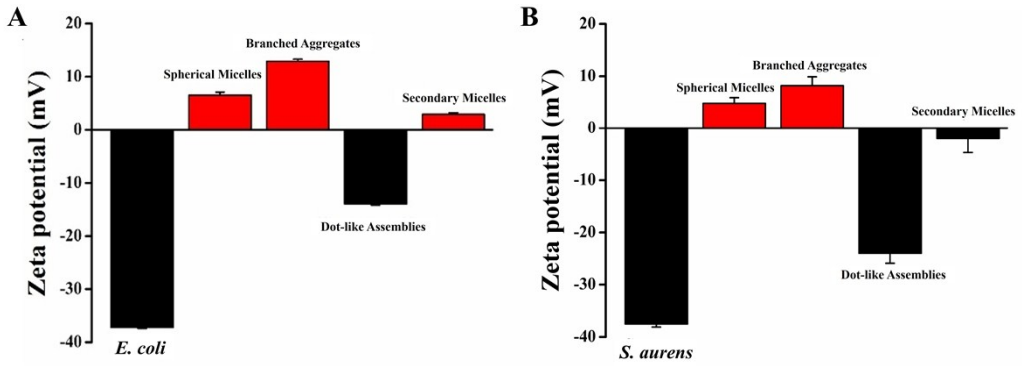


Fig. S19 Zeta potential values of assemblies co-cultured with (A) *E. coli* and (B) *S. aurens.*

6.5 SEM measurements

In order to further verify the difference in antibacterial results about assemblies with three specific morphologies, SEM was applied to characterize the changes in bacteria surface of treated by various assemblies. After the antibacterial experiments described above, *E. coli* and *S. aurens* were immediately collected by centrifugation. After removed the supernatant, the bacteria were treatment with 4% paraformaldehyde solution at room temperature overnight for bacterial

immobilization. Then, the bacteria were collected by centrifugation again. Next, the samples were washed three times with pure water and then were dehydrated by using ethanol in the gradient concentration (50% for 3 min, 70% for 3 min, 90% for 3 min, and 100% for 5 min). Then, 10 μL of the specimens were dropped onto silicon slices and drying in the air. Finally, the samples were gold-coated for SEM experiment.

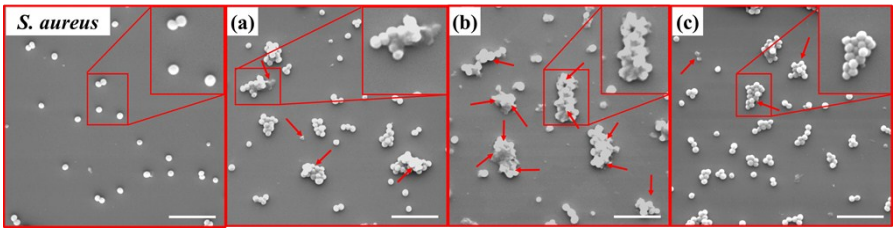


Fig. S20 SEM images of *S. aurens* (a) without treatment, (b) treated with spherical micelles, (c) branched aggregates, (d) dot-like assemblies. The red arrows in pictures indicate the destruction and collapse of cell membranes, Scale bars: 5μm.

6.6 TEM, DLS and the antibacterial efficiency of Fc-$(CD)_2$ self-assemblies

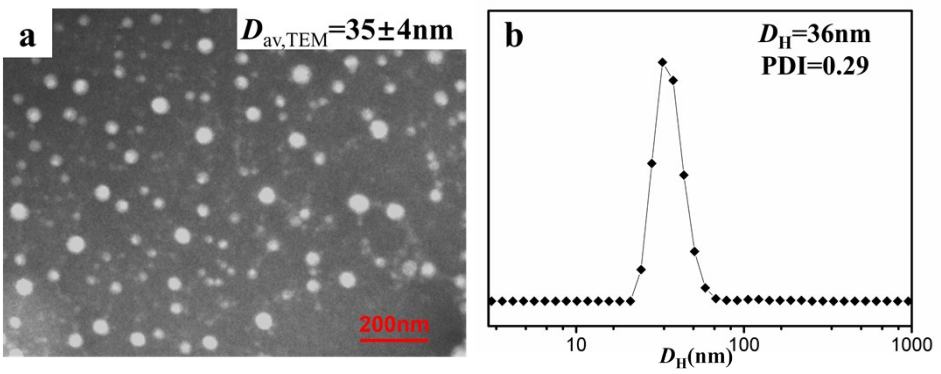


Fig. S21 Typical TEM image (a) and DLS curve (b) of Fc-$(CD)_2$ self-assemblies.

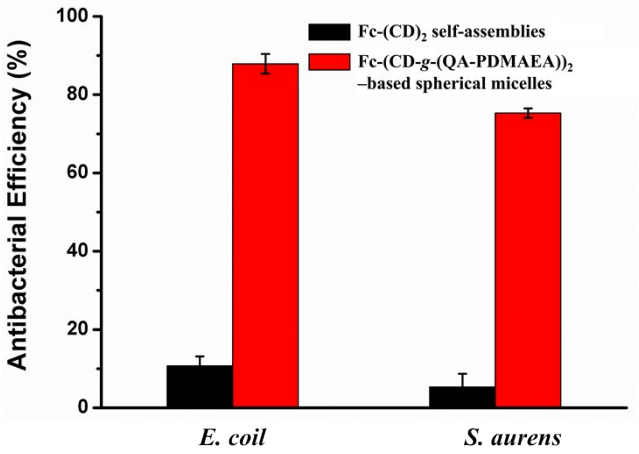


Fig. S22 The antibacterial efficiency toward to *E. coli* and *S. aurens* of Fc-$(CD)_2$ self-assemblies

and Fc-(CD-*g*-(QA-PDMAEA))$_2$-based on spherical micelles. Concentration=128 μg mL^{-1}.

6.7 Cell membrane permeability study by physical loaded

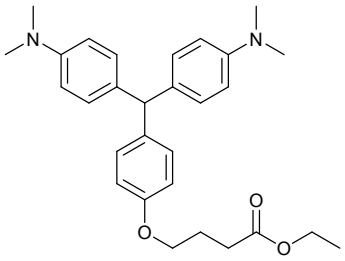


Fig. S23 Chemical Structure of FAP probe MG.

6.8 Controlled release of MG in branched aggregate

The Fc-(CD-*g*-(QA-PDMAEA)) was dissolved in water, and ultrasonicated for 15 minutes to obtain the assembly of branched aggregate. Then, MG solution (20μL, 1 mM, DMF) was slowly dropped by stirring to ensure thoroughly mixed. Next, the mixed solution was dialyzed (molecular weight cut off: 1000) 2 hours to remove DMF and unloaded MG molecules. Finally, the product was placed in PBS (pH 7.4) and shaken at 37 ^{o}C, and sampled was taken every 15 min. The resulting solution was co-incubated with *E. coli* (OD = 1.0), and the amount of released MG molecules was detected by fluorescence (Ex = 620 nm).

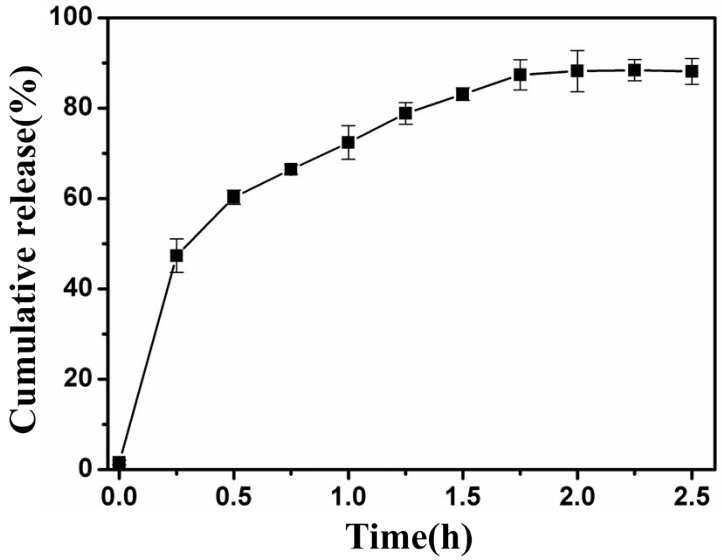


Fig. S24 Cumulative release curves of MG-loaded branched aggregates.

7. References

[S1] H.-T. Zhang, X.-D. Fan, W. Tian, R.-T. Suo, Z. Yang, Y. Bai and W.-B. Zhang, *Chem. Eur. J*., 2015, **21**, 5000-5008.

[S2] C.-G. Mu, X.-D. Fan, W. Tian, Y. Bai and X. Zhou, *Polym. Chem.,* 2012, **3**, 1137-1149.