

Supporting Information

Water-soluble supramolecular polymers fabricated through specific interactions between cucurbit[8]uril and tripeptide of Phe-Gly-Gly

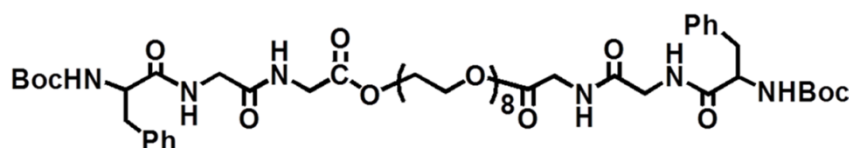
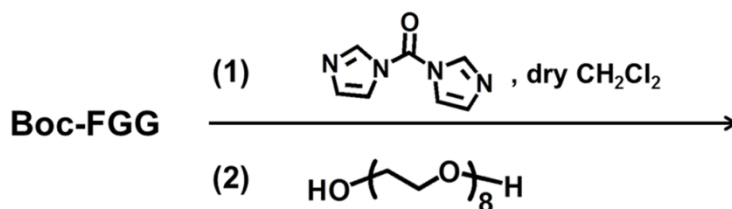
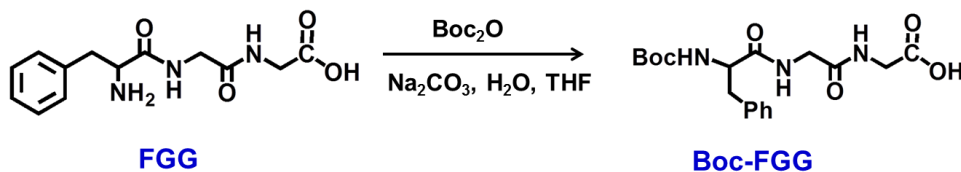
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1. Experimental Section

Materials preparation:

Boc-FGG: FGG 1.53 g (5.5 mmol) was dissolved into 8 mL 0.51 M Na₂CO₃ aqueous solution, and then 10 mL THF containing 1.87 g Boc₂O (8.58 mmol) was added drop wise into it under ice-cold with stirring. After 30 min, the mixture was warm to room temperature, and then it was stirred for 12 h. Most of THF was removed in vacuum and hydrochloric acid was added into the solution to acidification to pH 1, and a lot of white precipitate produced. The solution was extracted with ethyl acetate (5×25 mL). The organic phase were combined, dried over MgSO₄ and filtered. After concentration *in vacuo*, the product was purified by column chromatography (silica, CH₂Cl₂-CH₃OH 10:1) to give the product (1.85 g, 89.2%) as a white powder. ¹H NMR (JOEL JNM-ECA400, 400 MHz, CD₂Cl₂, 25 °C): δ (ppm) = 7.43~7.6 (5H), 7.05 (1H), 6.93 (1H), 5.20 (1H), 4.34 (1H), 3.96 (4H), 3.11 (1H), 2.97 (1H), 1.37 (9H).

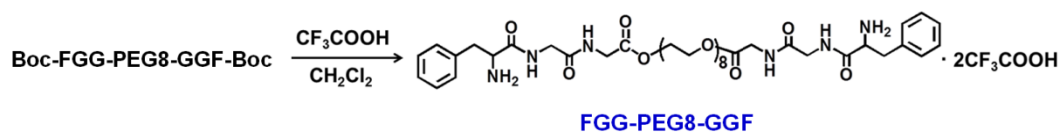


Boc-FGG-PEG8-GGF-Boc

Boc-FGG-PEG8-GGF-Boc: Boc-FGG 0.400 g (1.05 mmol) was dissolved into 25mL dry CH₂Cl₂, and then 0.202 g (1.25 mmol) N, N'-carbonyldiimidazole was added into the solution. The mixture was stirred for 12 h in N₂ atmosphere at room temperature, and a lot of white precipitate produced. Then 0.185 g (0.50 mmol) dry octaethylene glycol was added into the mixture. Then the mixture was stirred for 48 h in N₂ atmosphere at room temperature, and the white precipitate disappeared

gradually. Then 20 mL NaCl saturated solution (containing 1.0 mM HCl) was added into the CH_2Cl_2 solution. The solution was extracted with CH_2Cl_2 (5×25 mL). The organic phase were combined, dried over MgSO_4 and filtered. After concentration *in vacuo*, the product was purified by column chromatography (silica, CH_2Cl_2 – CH_3OH 10: 1) to give the product (0.518 g, 94.8%) as a colorless, transparent and sticky solid. ^1H NMR (JOEL JNM-ECA400, 400 MHz, CD_2Cl_2 , 25 °C): δ (ppm) = 7.25~7.18 (4H), 7.18~7.09 (6H), 7.06~6.82 (4H), 5.28 (2H), 4.24 (2H), 4.16 (4H), 3.98~3.83 (6H), 3.77 (2H), 3.59 (4H), 3.56~3.44 (24H), 3.05 (2H), 2.87 (2H), 1.28 (18H).

FGG-PEG8-GGF: Boc-FGG-PEG8-GGF-Boc 0.24g (0.22 mmol) was stirred in CF_3COOH – CH_2Cl_2 (1:1, 5 mL) for 4 h, at room temperature. The solvent was removed *in vacuo*, and then the obtained sticky solid was dissolved in 1 mL CH_3OH and precipitated in diethyl ether. The white precipitate was collected by filtration and washed with diethyl ether. The obtained product was further purified by HPLC. (Analytical injections were monitored at 214 nm, 254 nm. A SHIMADZU (Prominence LC-20AT) instrument using a semi preparative column (Grace Vydac “Peptide C18”, 250 X 10 mM, 10 μm particle size, flow rate 3 mL/min. Gradient: 5-70% $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ over 30 min.) After dried *in vacuum*, 0.15 g final product was obtained, yielding 58.3%. ^1H NMR (JOEL JNM-ECA400, 400 MHz, D_2O , 25 °C): δ (ppm) = 7.47~7.37 (6H), 7.33 (4H), 4.35 (4H), 4.32 (2H), 4.06 (4H), 4.01 (2H), 3.93 (2H), 3.81 (4H), 3.76~3.67 (24H), 3.31~3.19 (4H), as shown in Figure S1. ^{13}C NMR δ (ppm) = 171.30, 171.26, 169.86, 133.86, 129.48, 129.24, 138.27, 128.09, 69.69, 69.63, 68.39, 64.72, 54.55, 42.18, 41.22, 36.86, as shown in Figure S2. ESI: m/z 447.23 $[\text{M}+2\text{H}]^{2+}$, 893.45 $[\text{M}+\text{H}]^+$, 894.45 $[(\text{M}+1)+\text{H}]^+$, as shown in Figure S3.



ITC: ITC study was carried out with a Microcal VP-ITC apparatus at 298.15 K.

MALDI-TOF mass spectroscopy: MALDI-TOF mass spectroscopy study was carried out with an AXIMA Performance-MALDI TOF/TOF, and α -cyano-4-hydroxycinnamic acid was used as a matrix.

AFM-based single-molecule force spectroscopy: The commercially available V-shaped Si_3N_4 AFM cantilevers (Bruker, Santa Barbara, CA) with a sharp tip (radius of curvature 50 nm) at the end of a soft cantilever and a spring constant of 0.010-0.040 N/m were utilized in the experiment. Quartz wafers were treated with hot piranha solution (7:3 v/v 98% H_2SO_4 : 30% H_2O_2) for 1 hour, sonicated in large amounts of deionized water for several times, rinsed with ethanol, and dried in a steam of nitrogen. (**Caution:** piranha solution is very corrosive and can react violently with organics, so security measures should be taken.) The SMFS experiments were carried out utilizing a commercially available molecular force probe 3D (Asylum Research, Santa Barbara, CA) at room temperature. A solution of CB[8]–FGG-PEG8-GGF (2.0 mM) was mounted between the AFM tip holder and the freshly cleaned quartz wafer.

In brief, polymer chains could absorb onto the AFM tip as well as on the substrate to form the so-called polymer bridge. With the AFM tip separated from the substrate, the polymer bridge was stretched and the cantilever was deflected. The deflection of the cantilever and the extension were recorded simultaneously, and then converted to force–extension curves (in brief, force curves).

2. Characterization of FGG-PEG8-GGF

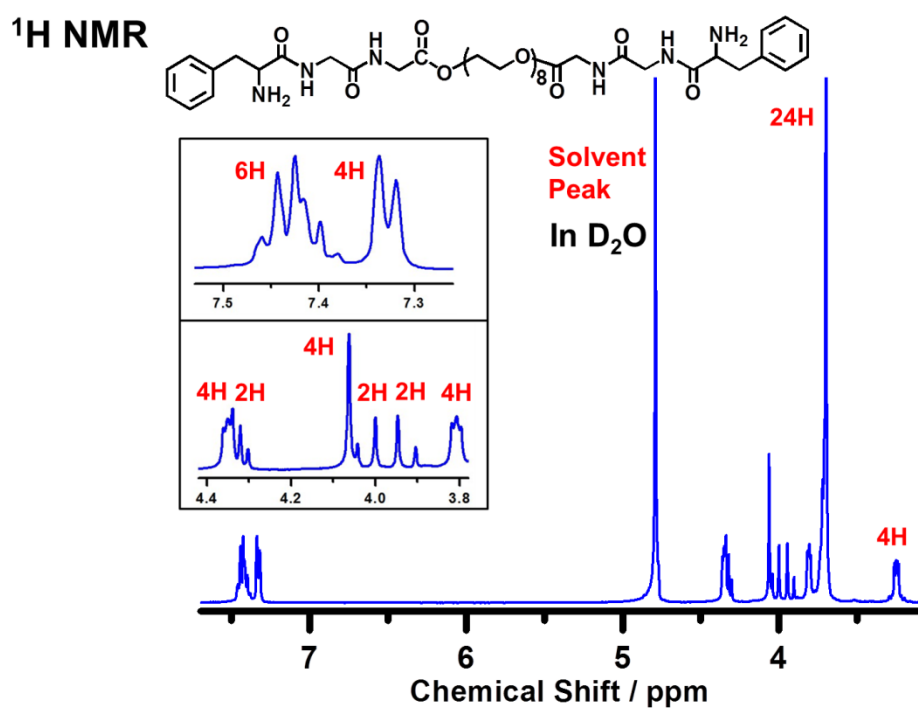


Figure S1. ¹H NMR spectrum of FGG-PEG8-GGF.

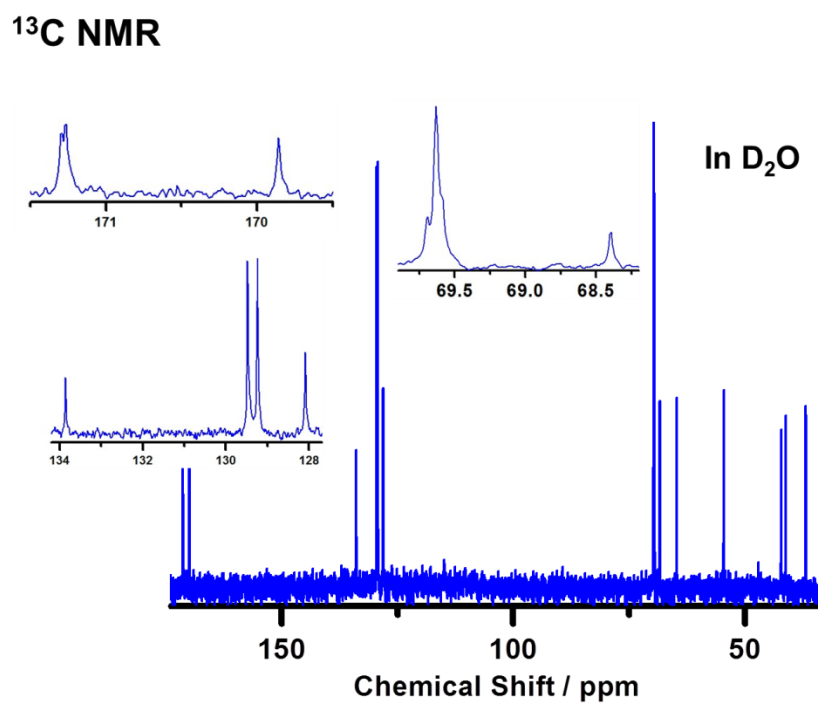


Figure S2. ¹³C NMR spectrum of FGG-PEG8-GGF.

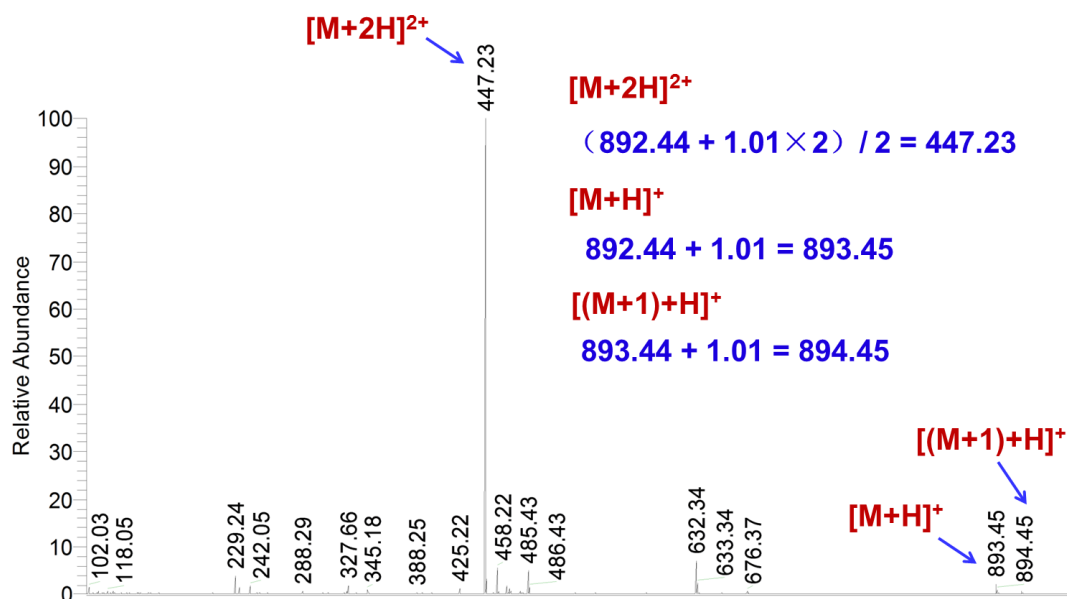


Figure S3. ESI Mass spectroscopy of FGG-PEG8-GGF.

3. Depolymerization of Supramolecular Polymers Formed by FGG-PEG8-GGF and CB[8].

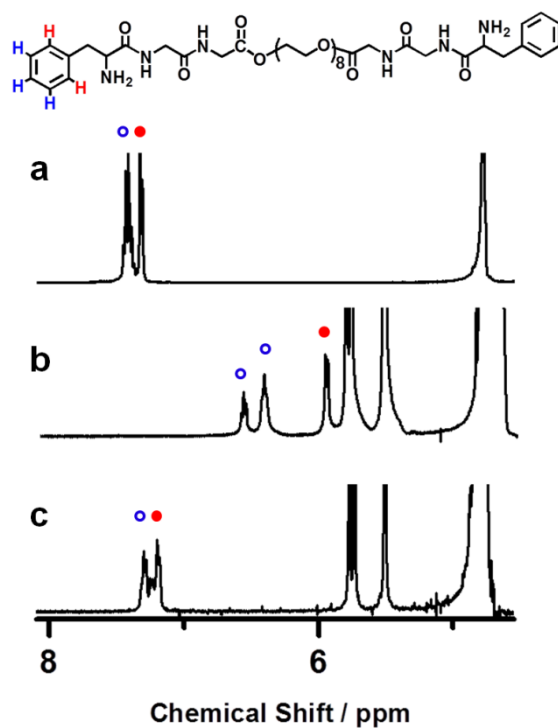


Figure S4 ^1H NMR spectra of a) the bifunctional monomer, FGG-PEG8-GGF, b) the supramolecular polymers formed by mixing FGG-PEG8-GGF and CB[8] (2 mM : 2 mM), and c) the depolymerized state with addition of 15 mM triethylamine in D_2O at 25 °C.