Supporting Information

Supramolecular polymerization of supramonomers: a way for fabricating supramolecular polymers

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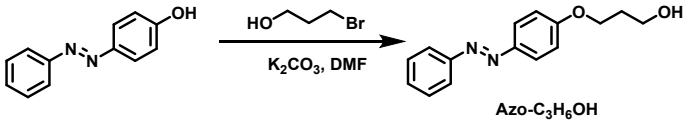
1. Experimental Section

Materials preparation:

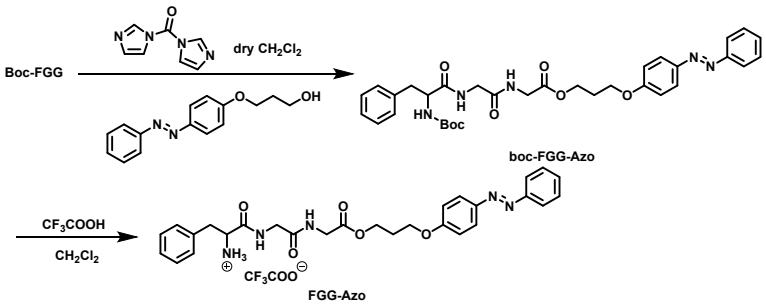
Azo-C_3H_6OH: 4-phenylazophenol 1.98 g (10 mmol) and 3-bromo-1-propanol 1.09 mL (12 mmol) were dissolved into 30 mL DMF, and potassium carbonate 2.07 g (15 mmol) was then added into the solution. After 12 h reaction at 75 °C in oil bath, the solution was poured into 50 mL water and extracted with 50 mL chloroform. After washed with 1 M HCl and saturated NaCl, the solution was dried with anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure after filtration to obtain a yellow solid. The crude product was purified via column chromatography (silica, ethyl acetate: dichloromethane=1:6) to give the product as an orange crystalline powder (1.55 g, yield: 60 %). ^{1}H NMR (JOEL JNM-ECA400, 400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.63 (1H), 2.11 (2H), 3.89 (2H), 4.21 (2H), 7.02 (2H), 7.47 (3H), 7.90 (4H).



Azo-C_3H_6OH

Boc-FGG-Azo: Boc-FGG 100 mg (0.264 mmol) was dissolved into 6 mL dry CH_2Cl_2 and N,N'-carbonyldiimidazole 50 mg (0.313 mmol) was then added into the solution. The mixture was stirred for 12 h at room temperature and lots of white precipitate appeared. Then 100 mg (0.390 mmol) AzoC_3H_6OH was added into the solution. The mixture was stirred for 48 h at room temperature to acquire an orange transparent solution. After mixed with 20 mL NaCl saturated solution (with 1 mM HCl), the solution was extracted with 100 mL acetic ether. Then the organic phase was dried with anhydrous $MgSO_4$ and filtered. The crude product obtained was an orange, sticky solid.

FGG-Azo: The crude Boc-FGG-Azo was stirred in CF_3COOH-CH_2Cl_2 (1:1, 5 mL) for 12h. The solvent was removed under reduced pressure and dissolved in 2 mL CH_3OH. After precipitated in diethyl ether, the crude product was collected by filtration. The product was finally 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: 5-60 % CH_3CN/H_2O over 30 min.) The obtained yellow power was characterized by ^{1}H NMR, ^{13}C NMR and ESI MS. ^{1}H NMR (JOEL JNM-ECA400, 400 MHz, D_2O, 25 °C) δ (ppm) = 2.10 (2H), 3.04 (2H), 3.80 (2H), 3.90 (2H), 4.15 (3H), 4.30 (2H), 7.06 (2H), 7.13 (2H), 7.23 (3H), 7.49 (3H), 7.73 (4H), as shown in Figure S1. ^{13}C NMR (JOEL JNM-ECA400, 100 MHz, CD_3OD, 25 °C) δ (ppm) = 171.48, 171.20, 170.17, 162.98, 154.09, 148.30, 135.64, 131.65, 130.46, 130.20, 130.16, 128.90, 125.75, 123.49, 115.90, 65.87, 63.14, 55.88, 42.89, 42.02, 38.48, 29.62, as shown in Figure S2. ESI: m/z 518.24 $[M+H]^+$, 540.22 $[M+Na]^+$, 556.20 $[M+K]^+$, as shown in Figure S3.



Methods: ^{1}H NMR, ^{13}C NMR and DOSY NMR were recorded on a JOEL JNM-ECA400 apparatus (400 MHz). UV-vis spectra were obtained using a HITACHI U-3010 spectrophotometer. Asymmetric Flow Field Flow Fractionation experiments (AsF-FFF) were performed by Wyatt Technology Eclipse 3+ with multi-angle light scattering detector (DAWN HELEOS-II), Ultraviolet and Differential Refraction detector (Optilab rEX). ESI mass spectra were recorded by Thermo Fisher DSQ.

AFM-based single-molecule force spectroscopy: The commercially available V-shaped Si3N4 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 supramolecular polymers (FGG-Azo: 4.0 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-Azo

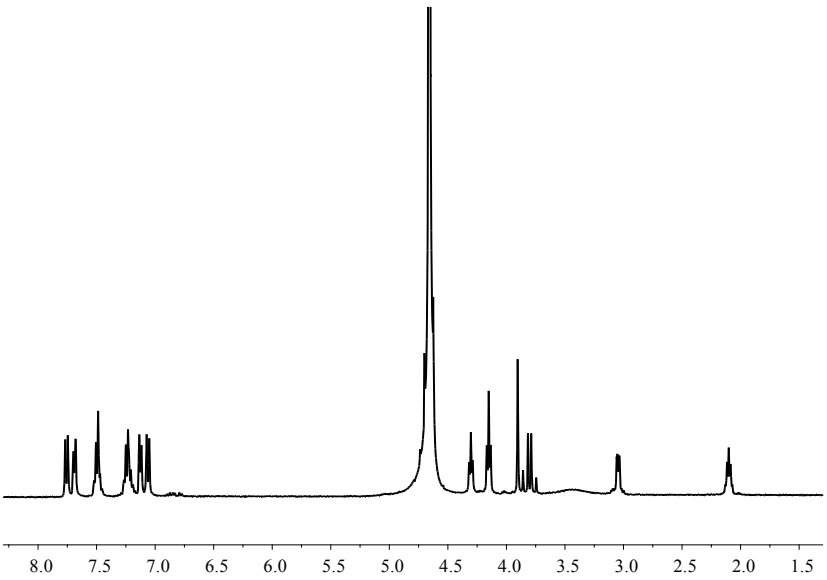


Figure S1 ^{1}H NMR spectrum of FGG-Azo (400 M, D_2O)

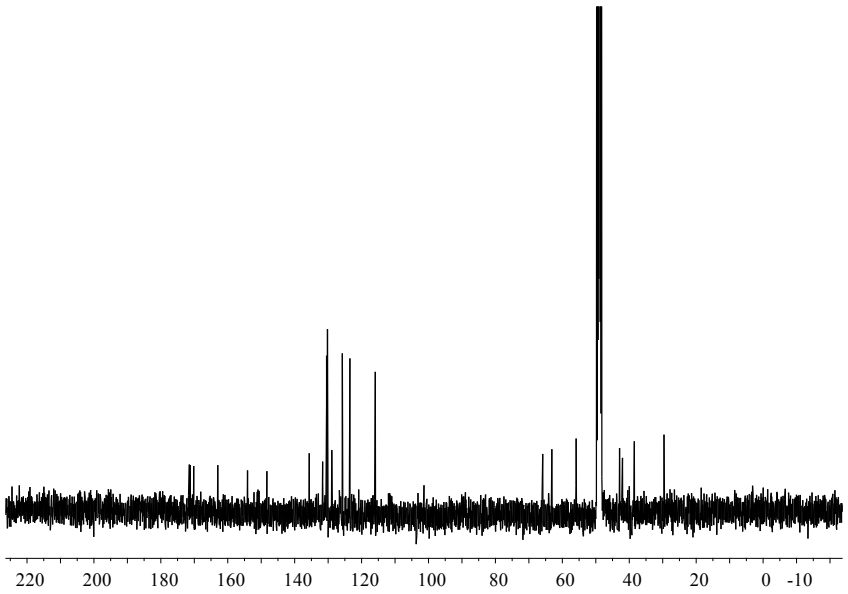


Figure S2. ^{13}C NMR spectrum of FGG-Azo (100 M, CD_3OD)

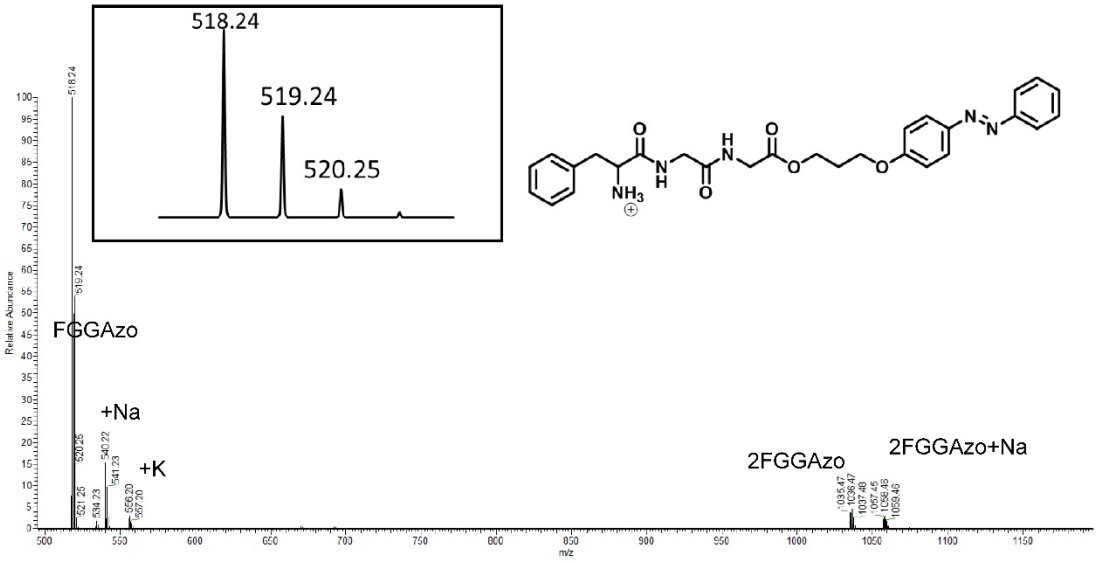


Figure S3 ESI mass spectrum of FGG-Azo

3. Formation of supramonomers

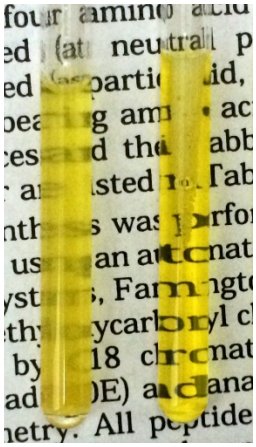


Figure S4 Photos of aqueous solution of FGG-Azo (left) and supramonomers (right)

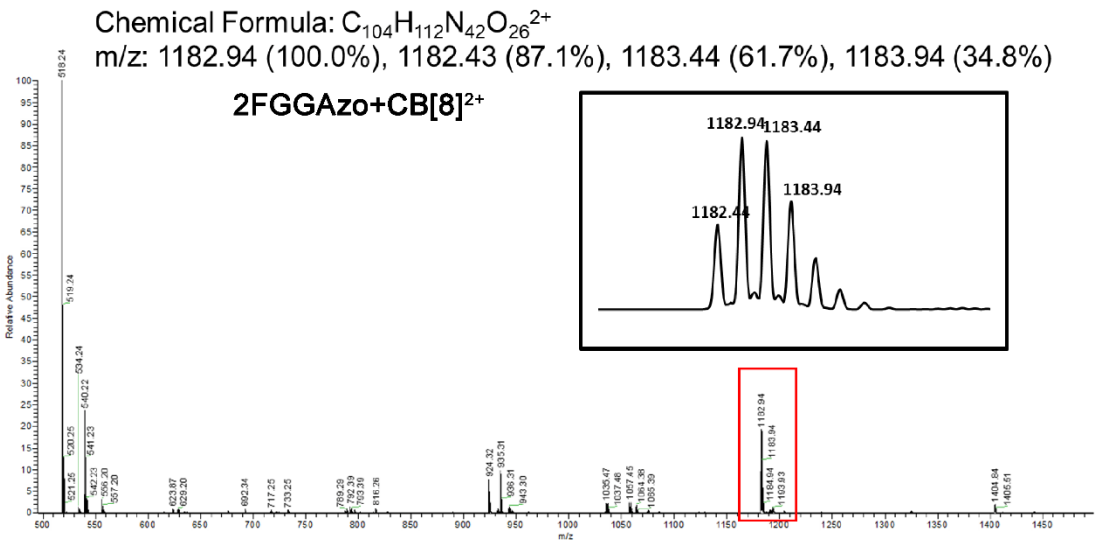


Figure S5 ESI mass spectrum of supramonomers

4. UV spectroscopic titration experiments

$$\Delta A = \frac{\alpha([H]_0 + [G]_0 + 1/K_s) \pm \sqrt{\alpha^2([H]_0 + [G]_0 + 1/K_s)^2 - 4\alpha^2[H]_0[G]_0}}{2}$$

Where Δ A is absorbance changes at 347 nm, $[G]_0$=[supramonomres]=0.05 mM, $[H]_0$=[bis-β-cyclodextrins], K_s is the binding constant between supramonomers and bis-β-cyclodextrins.

5. Formation of supramolecular polymers.

SMFS

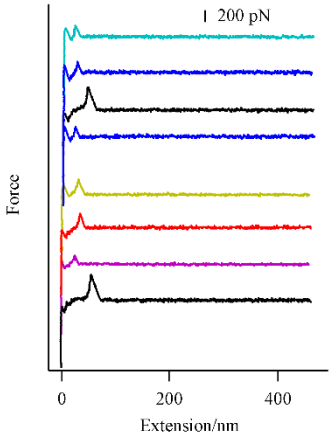


Fig. S6 Characteristic force-extension curves of supramolecular polymers.

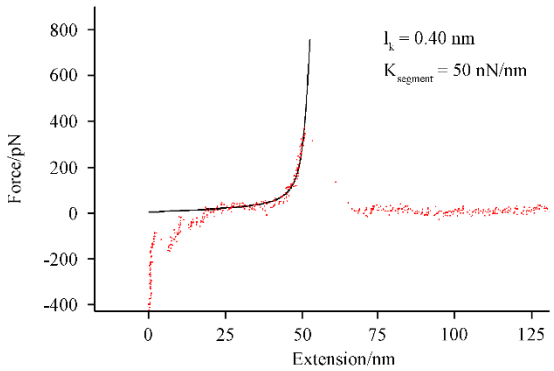


Fig. S7 Modified freely jointed chain (M-FJC) simulation. (l_k = 0.40 nm, $k_{segment}$ = 50 nN/nm)

6. Depolymerization of supramolecular polymers

Figure S8 Photos of solution of supramolecular polymers before (left) and after (right) adding triethylamine.

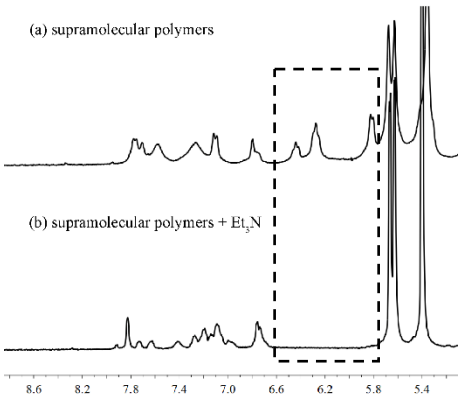


Figure S9 ^{1}H NMR of supramolecular polymers before (a) and after (b) adding triethylamine. (400 M, D_2O)

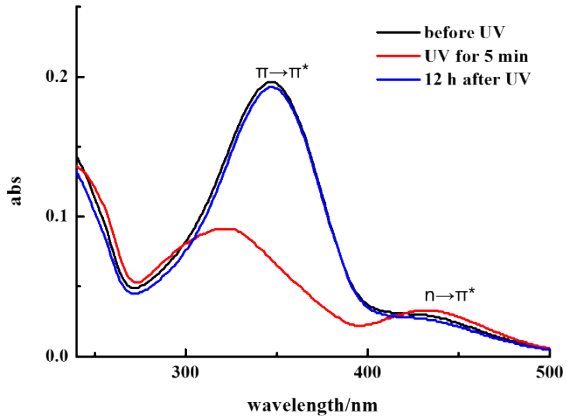


Figure S10 UV spectrum of supramolecular polymers before and after UV irradiation. (FGG-Azo: 0.1 mM)