# **Supporting Information**

## **Redox-switchable supramolecular polymers for responsive**

## self-healing nanofibers in water

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### **1. Experimental Section**

#### 1.1 Materials Preparation

#### β-CD-OEG-β-CD (Monomer Unit 1):



Mono-6-deoxy-6-ethylenediamine- $\beta$ -CD ( $\beta$ -CD-NH<sub>2</sub>, 1.880 g, 1.6 mmol, synthesized according to Reference S1), carboxyl group end-capping oligo(ethylene glycol) (HOOC-OEG-COOH, 0.320 g, 0.8 mmol, synthesized according to Reference S2), 1-ethyl-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, 0.300 g, 1.9 mmol), and *N*,*N*-dimethylamino-pyridine (DMAP, 23 mg, 0.19 mmol) were reacted in water at room temperature for 24 h. The white precipitate was filtered, and then the filtrate was washed with diethyl ether three times. The aqueous phase was precipitated by acetone and recrystallized in water for the final product. Yield: 62%. <sup>1</sup>H NMR (D<sub>2</sub>O,  $\delta$ , ppm), 4.94 (H-1 in  $\beta$ -CD), 4.37 (-NHCO-C**H**<sub>2</sub>-O-), 3.51–3.83 (-OC**H**<sub>2</sub>C**H**<sub>2</sub>O- and H-3,5,6 in  $\beta$ -CD), 3.21–3.34 (H-2,4 in  $\beta$ -CD), 2.79 (-C**H**<sub>2</sub>CH<sub>2</sub>NH- $\beta$ -CD), 2.54 (-CH<sub>2</sub>C**H**<sub>2</sub>NH- $\beta$ -CD). <sup>13</sup>C NMR (D<sub>2</sub>O,  $\delta$ , ppm): 171.5 (-NHCO-), 81.5 (H-4 in  $\beta$ -CD), 71.2 (H-5 in  $\beta$ -CD), 69.4 (-OCH<sub>2</sub>CH<sub>2</sub>O- in OEG), 60.8 (H-1 in  $\beta$ -CD), 57.7 (-OCH<sub>2</sub>CONH-), 48.2 (-CONHCH<sub>2</sub>CH<sub>2</sub>NH-), 47.1 (-CONHCH<sub>2</sub>CH<sub>2</sub>NH-), 39.5 (H-6 in  $\beta$ -CD). MALDI-TOF:  $M_w$  = 2714.



*Fig. S1.* The <sup>1</sup>H NMR spectrum of the monomer  $\beta$ -CD-OEG- $\beta$ -CD (D<sub>2</sub>O,  $\delta$  = 4.79)



*Fig. S2.* The <sup>13</sup>C NMR spectrum of the monomer  $\beta$ -CD-OEG- $\beta$ -CD (D<sub>2</sub>O)

OEG-β-CD (**Model Compound for ITC experiment**):



The model compound OEG- $\beta$ -CD for ITC experiments was synthesized by similar process with  $\beta$ -CD-OEG- $\beta$ -CD.  $\beta$ -CD-NH<sub>2</sub> (1.180 g, 1.0 mmol), mono-carboxyl terminal OEG (OEG-COOH, 0.398 g, 1.0 mmol), 1-ethyl-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, 0.190 g, 1.2 mmol), and *N*,*N*-dimethylamino-pyridine (DMAP, 15 mg, 0.12 mmol) were reacted in water at room temperature for 24 h. The white precipitate was filtered, and then the filtrate was washed by diethyl ether for three times. The aqueous phase was precipitated by acetone and recrystallized in water to afford the final product. Yield: 84%. <sup>1</sup>H NMR (D<sub>2</sub>O,  $\delta$ , ppm), 4.91 (H-1 in  $\beta$ -CD), 4.36 (-NHCO-C $H_2$ -O-), 3.51–3.81 (-OC $H_2CH_2O$ - and H-3,5,6 in  $\beta$ -CD), 3.31–3.47 (-OC $H_3$  and H-2,4 in  $\beta$ -CD), 2.79 (-C $H_2$ CH<sub>2</sub>NH- $\beta$ -CD), 2.47 (-CH<sub>2</sub>C $H_2$ NH- $\beta$ -CD). <sup>13</sup>C NMR (D<sub>2</sub>O,  $\delta$ , ppm): 171.2 (-NHCO-), 80.2 (H-4 in  $\beta$ -CD), 71.3 (H-5 in  $\beta$ -CD), 69.8 (-OCH<sub>2</sub>CH<sub>2</sub>O- in OEG), 60.1 (H-1 in  $\beta$ -CD), 59.7 (-OCH<sub>2</sub>CONH-), 57.6 (-OCH<sub>3</sub>), 49.2 (-NHCH<sub>2</sub>CH<sub>2</sub>NH-), 46.5 (-CONHCH<sub>2</sub>CH<sub>2</sub>NH-), 39.5 (H-6 in  $\beta$ -CD). MALDI-TOF:  $M_w$  = 1631.

Fc-OEG-Fc (Monomer Unit 2):



Ferrocenylcarboxylic acid (Fc-COOH, 1.380 g, 6.0 mmol), oligo(ethylene glycol) (OEG,  $M_w$  = 350 g/mol, 0.875 g, 2.5 mmol), dicyclohexylcarbodiimide (DCC, 1.240 g, 6 mmol), and DMAP (74 mg, 0.6 mmol) were reacted in 50 mL CH<sub>2</sub>Cl<sub>2</sub> at 0 °C for 2 h and then at 25 °C for overnight under nitrogen atmosphere. The byproduct was removed by filtration, and the filtered solution was removed by rotary evaporator. The yellow crude products were dissolved in 30 mL of water and extracted by diethyl ether (20 mL×3). The organic phase was dried with anhydrous magnesium sulfate (MgSO<sub>4</sub>) and the solvent was removed to get the pure product. Yield: 77%. <sup>1</sup>H NMR

(CDCl<sub>3</sub>,  $\delta$ , ppm), 4.88, 4.45, and 4.24 (9H, protons in ferrocenyl), 4.33 (4H, Fc-COOCH<sub>2</sub>CH<sub>2</sub>-), 3.68 (28H, -OCH<sub>2</sub>CH<sub>2</sub>O-). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 169.9 (Fc-COOCH<sub>2</sub>-), 72.1, 70.8, 70.2, 67.1 (in the ferrocenyl), 69.4 (-OCH<sub>2</sub>CH<sub>2</sub>O-), 57.6 (-COOCH<sub>2</sub>-). MALDI-TOF:  $M_w$  = 794.



*Fig. S3.* The <sup>1</sup>H NMR spectrum of the monomer Fc-OEG-Fc (CDCl<sub>3</sub>,  $\delta$  = 7.26)





#### OEG-Fc (Model Compound for ITC experiment):



The synthetic process was similar with Fc-OEG-Fc. Ferrocenylcarboxylic acid (Fc-COOH, 0.460 g, 2.0 mmol), mono-hydroxyl oligo(ethylene glycol) (OEG,  $M_w$  = 350 g/mol, 0.700 g, 2.0 mmol), dicyclohexylcarbodiimide (DCC, 0.770 g, 2.2 mmol), and DMAP (25 mg, 0.2 mmol) were reacted in 30 mL CH<sub>2</sub>Cl<sub>2</sub> at 0 °C for 2 h and then at 25 °C for overnight under nitrogen atmosphere. The byproduct was removed by filtration, and the filtered solution was removed by rotary evaporator. The yellow crude products were dissolved in 25 mL of water and extracted by diethyl ether (20 mL×3). The organic phase was dried with anhydrous magnesium sulfate (MgSO<sub>4</sub>) and the solvent was removed to obtain the yellow product. Yield: 82%. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm), 4.87, 4.29, and 4.18 (9H, protons in ferrocenyl group), 4.35 (4H, Fc-COOCH<sub>2</sub>CH<sub>2</sub>-), 3.68 (28H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.51 (3H, -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 169.2 (Fc-COOCH<sub>2</sub>-), 72.4, 70.6, 70.2, 67.2 (in the ferrocenyl), 69.6 (-OCH<sub>2</sub>CH<sub>2</sub>O-), 57.6 (-COOCH<sub>2</sub>-), 55.8 (-OCH<sub>3</sub>). MALDI-TOF:  $M_w$  = 596.

#### 1.2 Characterization

UV-Vis Spectroscopy: UV-Vis spectra were obtained by a HITACHI U-3010 spectrophotometer.

*ITC experiment*: The ITC experiment was carried out using a Microcal VP-ITC apparatus. The measurements were performed in pH 7.2 phosphate buffer solution at 298.15 K.

*Nuclear Magnetic Resonance (NMR):* <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for the polymer structural analysis were obtained from JEOL JNM-ECA400 (400 MHz) and JEOL JNM-ECA600 (600 MHz) spectrometer. The solvent was CDCl<sub>3</sub> ( $\delta_{CDCl3}$  = 7.26) and D<sub>2</sub>O ( $\delta_{D2O}$  = 4.79).

*Transmission Electron Microscopy (TEM):* The visualized images of the assemblies were obtained from a JEOL JEM-2010 Microscope with an accelerating voltage of 120 kV. In the experiment of redox-responsive assembly and disassembly of supramolecular nanofibers, we used pipette to absorb 20  $\mu$ L of solution near the electrode in the electrolytic cell in a fix time interval of 5 min. Then they were dropped onto a piece of cupper grid and the sample was quickly stained by 0.2% phosphotungstic acid hydrate. Before observation, these grids were freeze-drying in the liquid nitrogen atmosphere for 5 min in order to stabilize the morphologies of these supramolecular nano-objects.

*Viscosity Measurement:* Rheology analysis was monitored by using an AR-G2 Rheometer (TA Instruments) with 40 mm parallel plate geometry.

*Electrochemical Measurement:* Cyclic voltammetry (CV) measurement was carried out using a potentionstat (Autolab PGSTAT12) in a conventional three-electrode glass electrochemical cell at ambient temperature by taking Ag/AgCl (saturated KCl) electrode as reference electrode, a bare platinum plate electrode selected as a working electrode, and platinum wire as a counter electrode. The electrolyte solution is  $0.10 \text{ M NH}_4\text{PF}_6$  aqueous solution.

### 2. Supportive Evidence and Results

2.1 Static Light Scattering (SLS) for Fc-OEG-Fc/β-CD-OEG-β-CD Supramolecular Polymer Molecular Weight Characterization



*Fig. S5.* The curve of apparent molecular weight  $(M_{w,app})$  versus the concentration of Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD. The two monomers are fixed on 1:1 molar ratio.

The apparent molecular weight  $(M_{w,app})$  was monitored by static light scattering (SLS). It offers us supportive evidence about the degree of supramolecular polymerization at different concentrations. When Fc-OEG-Fc and  $\beta$ -CD-OEG- $\beta$ -CD was equally blended at low concentration (1.0 mM), the molecular weight is approximately 4.1 kDa with the polydispersion index of 2.18, which is consistent with the  $M_{w,app}$  of a cyclic Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD dimer and trimer; in contrast,

while mixing at high concentration (20 mM), the molecular weight had an abrupt increase to 89.2 kDa with the polydispersion index of 2.83, corresponding to a supramolecular polymer with the degree of polymerization,  $n \approx 25$  (**Fig. S5**). These results further demonstrate that the Fc-OEG-Fc and  $\beta$ -CD-OEG- $\beta$ -CD can self-assemble into high molecular weight noncovalently linear polymer through the Fc/ $\beta$ -CD host-guest recognition.

#### 2.2 The Mechanism Explanation of Electrochemical Redox for Supramolecular Polymers

Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD supramolecular polymers can spontaneously form from two ditopic monomers, Fc-OEG-Fc and  $\beta$ -CD-OEG- $\beta$ -CD, based on the Fc/ $\beta$ -CD host-guest interactions. This noncovalent polymerizable reaction is dynamic and reversible equilibrium reaction as **Eq. (1)**. The host-guest association constant ( $K_t$ ) is much more than the dissociation constant ( $K_d$ ). If we supposed that the initial concentration of two monomers are both 1.0 mM, according to the value of  $K_t$  by ITC data ( $K_t = 4.92 \times 10^4 \text{ M}^{-1}$ ) the final concentration of Fc-OEG-Fc is approximately 0.045 mM from **Eq. (2)**. It indicates that great amount of monomers have formed supramolecular adducts and there are only a small quantity of free Fc-OEG-Fc and  $\beta$ -CD-OEG- $\beta$ -CD monomers existing in solution.



*Fig. S6.* Schematic illustration of electrochemical oxidation mechanism of the Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD supramolecular polymer

To study the electrochemical redox-responsivity of Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD supramolecular polymer, we attempted to electrochemically control the Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD polymers. The supramolecular polymer was electrolyzed with a potentiostat using a three-electrode system (Ag/AgCl (reference), platinum plate (working), platinum wire (counter)) and 0.10 M of  $NH_4PF_6$ as a supporting electrolyte. From the experimental results, upon an oxidative potential (+0.5 V), Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD can disassemble into monomers; reversibly, monomeric units can re-assemble into polymer structure under reductive potential condition (-0.5 V). The mechanism of redox-controlled assembly and disassembly of supramolecular polymer can divide into three steps: Initially, there are three kinds of compounds in aqueous solution including a small amount of free Fc-OEG-Fc and  $\beta$ -CD-OEG- $\beta$ -CD and majority of Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD polymers. In the electrochemical oxidative process, (i) free Fc-OEG-Fc species in solution is readily oxidized into charged species  $Fc^+$ -OEG- $Fc^+$ , while Fc-OEG- $Fc/\beta$ -CD-OEG- $\beta$ -CD supramolecular polymer is difficult to electrochemically oxidize due to the strong protection of host-guest inclusion effect;<sup>S3</sup> (ii) When we applied a +0.5 V potential to the supramolecular polymer solution to electrolyze, the anodic reaction is that the free Fc-OEG-Fc on the surface of platinum electrode lost two electrons to change into the  $Fc^+$ -OEG- $Fc^+$  as *Eq.* (3); (iii) Along with the continuous oxidation and the decrease of free Fc-OEG-Fc concentration, the chemical equilibrium of Eq. (1) tends to left direction, leading to a consecutive dissociation of Fc-OEG-Fc/β-CD-OEG-β-CD supramolecular polymers into new Fc-OEG-Fc and  $\beta$ -CD-OEG- $\beta$ -CD monomers (Fig. S6). Finally, the polymers are completely disassembled. On the contrary, in the electrochemical reductive process (-0.5 V), the solution initially contains a great amount of free Fc<sup>+</sup>-OEG-Fc<sup>+</sup> species and  $\beta$ -CD-OEG- $\beta$ -CD monomers. The cathodic reaction is that the Fc<sup>+</sup>-OEG-Fc<sup>+</sup> reversibly transforms to Fc-OEG-Fc species. The increase of Fc-OEG-Fc concentration promotes the equilibrium of Eq. (1) to move right, resulting in the reformation of Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD supramolecular polymers.

2.3 UV-Vis Spectra of Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD Complex for the Host-Guest Association Constant



*Fig. S7.* The UV absorption of  $\beta$ -CD-OEG- $\beta$ -CD upon stepwise addition of Fc-OEG-Fc, the concentration of Fc-OEG-Fc keeps  $1 \times 10^{-5}$  M

The association constant between Fc-OEG-Fc and  $\beta$ -CD-OEG- $\beta$ -CD in aqueous solution was determined by following UV-Vis absorption at 274 nm, which is the characteristic absorption of Fc species. The concentration of Fc-OEG-Fc was kept at  $1 \times 10^{-5}$  M. Upon gradual addition of the  $\beta$ -CD-OEG- $\beta$ -CD moiety, the absorption of binary mixture increased remarkably. With formation of a simple 1:1 molecular adduct, the inclusion complexation of Fc-OEG-Fc/ $\beta$ -CD-OEG- $\beta$ -CD is expressed by the following equation:<sup>S4</sup>

$$H + G \xrightarrow{K_t} H \cdot G$$

We employed the usual double reciprocal plot according to the modified Hidebrand-Benesi equation:

$$\frac{1}{\Delta A} = \frac{1}{Kt\Delta\varepsilon[H][G]} + \frac{1}{\Delta\varepsilon[H]}$$

Where H, G,  $K_t$  represents as host Fc-OEG-Fc, guest  $\beta$ -CD-OEG- $\beta$ -CD, and association constant respectively.  $\Delta A$  denotes the absorbance difference before and after addition of  $\beta$ -CD-OEG- $\beta$ -CD species.  $\Delta \varepsilon$ , which denotes the difference of the molar extinction coefficient between the host and host-guest complex at the same wavelength, is  $4.73 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  in our work. The association constant  $K_t$  calculated by the equation is  $3.84 \times 10^4 \text{ M}^{-1}$ , which is consistent with the data of ITC measurements ( $K_t = 4.92 \times 10^4 \text{ M}^{-1}$ ), as shown in **Fig. S7**.

### References

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