

Supporting information for:

Fabrication of a β -cyclodextrin-based self-assembly containing a redox-responsive ferrocene

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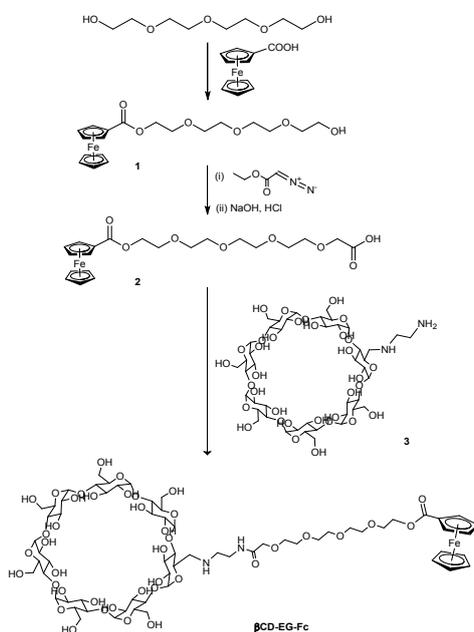
Synthesis of β CD-EG-Fc

β CD-EG-Fc was designed and synthesized as demonstrated in Scheme S1. Compound **1** was synthesized by the following procedure: ferrocenecarboxylic acid (2.06 g, 8.95 mmol) was dispersed in CH_2Cl_2 (100 mL), and then oxalyl chloride (2.3 mL, 26.9 mmol) was added slowly. The mixture was stirred at room temperature for 3 h resulting in a dark red solution. The solution was evaporated under vacuum giving a red oil (chlorocarbonyl ferrocene). The red oil was dissolved in THF (100 mL) and added dropwise into a solution of triethylene glycol (8.75 g, 45 mmol), DMAP (0.12 g, 1 mmol), TEA (6.24 mL, 44.7 mmol) and THF (400 mL) at 0 °C under N_2 . The mixture was then stirred at room temperature overnight. After the reaction was completed, the solvent was evaporated under vacuum giving an oil, which was purified by column chromatography (eluent: ethyl acetate/petroleum ether, v/v=1/3) giving compound **1** as a red oil. ¹H NMR ($\text{DMSO}-d_6$): δ (ppm): 4.75, 4.49, 4.29, 4.25 (m, 9H, protons of the cyclopentadienyl ring), 4.56 (t, 2H, Fc-COO- CH_2 - CH_2 -), 3.70, 3.61-3.47, 3.40 (m, 14H, - $(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ -OH); MS (ESI): calc. for $\text{C}_{19}\text{H}_{26}\text{FeO}_5$ ($[\text{M}]^+$): 406.11; found: 406.9 ($[\text{M}+\text{H}]^+$).

Compound **2** was synthesized according to the literature procedure.³² ¹H NMR ($\text{DMSO}-d_6$): δ (ppm): 4.76, 4.50, 4.23 (m, 9H, protons of the cyclopentadienyl ring), 4.29 (t, 2H, Fc-COO- CH_2 -); 4.00 (s, 2H, - OCH_2COOH); 3.45-3.70 (m, 14H, - $(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$ -O-). Compound **3** was synthesized in accordance with our previous report.³³ ¹H NMR (D_2O): δ (ppm): 5.07(s, 7H, H1 of CD), 4.02-3.53 (m, 40H, H2-6 of CD),

3.07-2.83 (t, 6H, $-\text{CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$).

Compound **2** (0.1 g, 0.22 mmol) was dissolved in CH_2Cl_2 (100 mL), and oxalyl chloride (0.057 mL, 0.67 mmol) was added slowly. The mixture solution was stirred for 3 h at room temperature. After the reaction was completed, the solvent was removed by vacuum distillation giving a brown solid. This was dissolved in DMF (50 mL), which was added slowly to a solution of compound **3** (0.2435 g, 0.207 mmol), TEA (0.288 mL) and DMF (100 mL) at 0 °C. The light yellow solution was stirred at room temperature overnight. The resultant solution was poured into cold acetone and placed in the refrigerator overnight resulting in a brown precipitate. The brown solid was collected and dried in a vacuum oven, furnishing the pure product, $\beta\text{CD-EG-Fc}$. $^1\text{H NMR}$ (D_2O): δ (ppm): 5.32 (d, 9H, protons of the cyclopentadienyl ring); 5.01 (s, 7H, H1 of CD), 4.31 (t, 4H, $-\text{NH-CO-CH}_2\text{-O-}$, $\text{Fc-COOCH}_2\text{-}$), 3.90-3.28 (m, 56H, $-\text{CH}_2\text{-NH-CO-}$, $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_2\text{-O-}$ and H2-6 of CD), 2.79, 2.93 (t, 4H, $-\text{CH}_2\text{-NH-CH}_2\text{-}$); MS (MALDI-TOF): calc. for $\text{C}_{65}\text{H}_{102}\text{FeN}_2\text{O}_{41}$ ($[\text{M}]^+$): 1622.53; found: 1645.52 ($[\text{M}+\text{Na}]^+$), 1623.54 ($[\text{M}+\text{H}]^+$).



Scheme S1 Synthesis of $\beta\text{CD-EG-Fc}$.

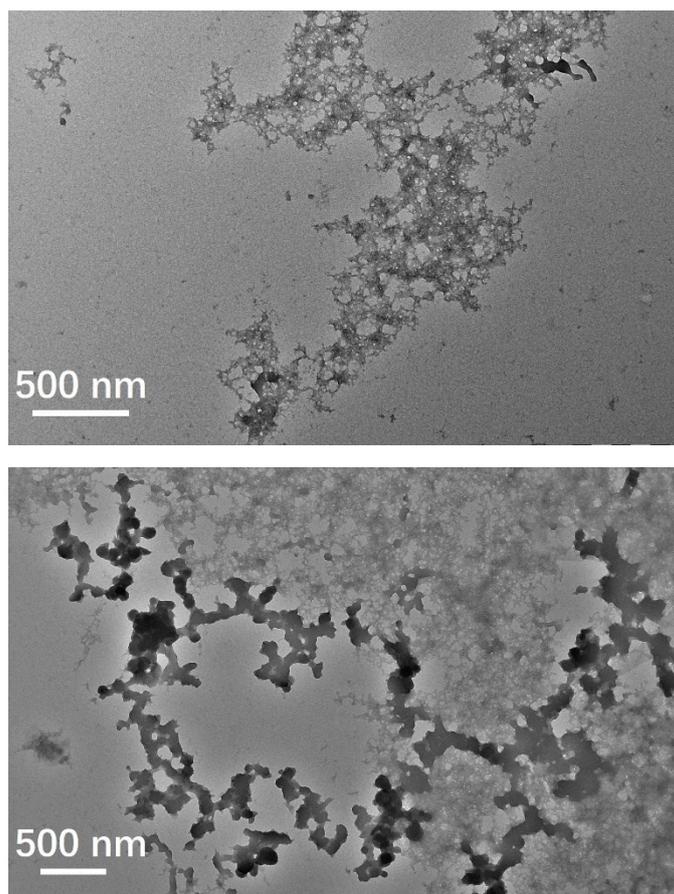


Fig. S1 TEM images of β CD-EG-Fc⁺ solution after the addition of GSH.

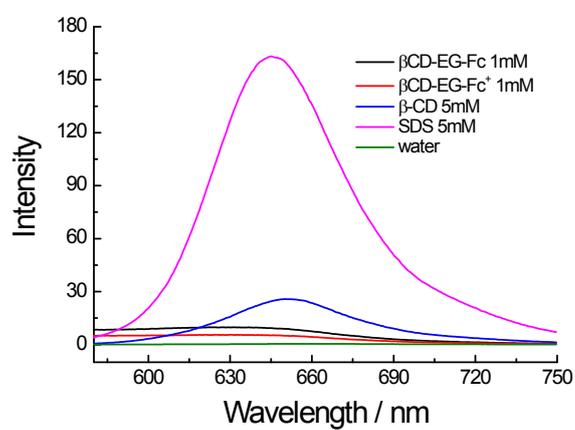


Fig. S2 Fluorescence spectra of Nile red solution, β CD-EG-Fc/ β CD-EG-Fc⁺ solution (1mM), β -CD solution (5mM), and SDS solution (5mM).