

Supplementary Information

Voltage-responsive single-chain polymer nanoparticles via host-guest interaction

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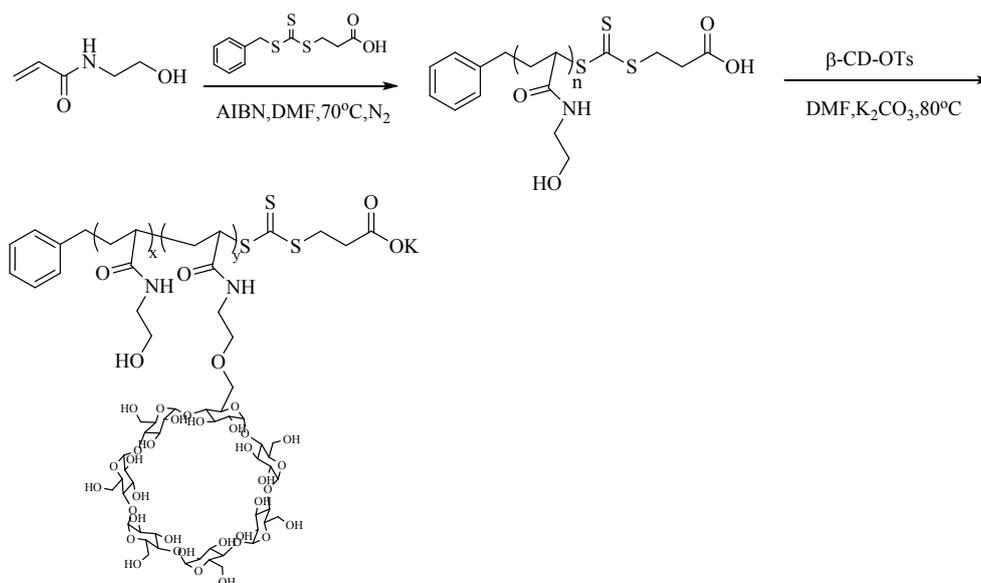
S.1 Materials

Ferrocenecarboxylic acid, ethyldiisopropylamine, p-toluenesulfonyl chloride, β -cyclodextrin, and 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate were obtained from Energy Chemical Co.. N-(2-hydroxyethyl) acrylamide and 1,8-diamino-3,6-dioxaoctane were obtained from J & K Chemical Co.. N,N-dimethyl formamide (DMF), 2,2'-azobisisobutyronitrile (AIBN), chloroform, acetone, ethanol, sodium hydroxide, sodium sulfate, and other chemicals were all analytical grade and purchased from Shanghai Chemical Reagent Co.. N-(2-hydroxyethyl) acrylamide was purified by alkaline aluminum oxide column chromatography. AIBN was recrystallized from ethanol. All other reagents were used without further purification. β -Cyclodextrin was recrystallized two times from water before using. DMF was dried via calcium hydride for two days and then distilled under a reduced pressure prior to use. Mono-6-deoxy-6-(p-tolylsulfonyl)- β -cyclodextrin (β -CD-OTs) and 3-benzylsulfanylthiocarbonylsulfanylpropionic acid (RAFT agent) were synthesized according to the method in literature, respectively.¹

S.2 Experimental Methods

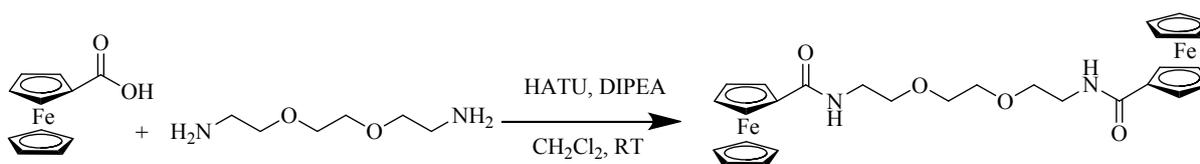
General synthesis of PHEAm. N-Hydroxyethylacrylamide (3.45 g, 30 mmol), RAFT agent (16.3 mg, 0.06 mmol) (Target $DP=[M]/[I]=500$), and AIBN (2 mg, 0.012 mmol) were dissolved in 12 mL DMF. The solution was degassed by bubbling nitrogen for 15 min and then placed in oil at 65 °C for 24 h. Subsequently, the mixture of the polymerization was diluted with DMF and precipitated in excess acetone. The solid was filtered and dried under vacuum, yielding the title compound as a white powder (2.76 g, yield: 80%).

General synthesis of PHEAm- β -CD. PHEAm (1.0 g, 8.6 mmol relative to hydroxyl functionality), mono-6-deoxy-6-(p-tolylsulfonyl)- β -cyclodextrin (1.02 g, 7.9 μ mol), and 0.5 g K_2CO_3 were suspended in 10 mL anhydrous DMF. The mixture was placed in oil at 80 °C for 24 h. Subsequently, the mixture was dialyzed with water for 3 days and then treated with freeze-drying.



Scheme S1 Synthesis of PHEAAm and PHEAm-β-CD

Synthesis of 1,8-diamino-3,6-dioxaoctane bridged bis(ferrocene). Ferrocenecarboxylic acid (1.15 g, 5 mmol), 1,8-diamino-3,6-dioxaoctane (0.37 g, 2.5 mmol), 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU) (4.2 g, 6 mmol), and N,N-diisopropylethylamine (DIPEA) (1.29 g, 10 mmol) were dissolved in 50 mL dried CH_2Cl_2 and then reacted at room temperature for 12 h. Subsequently, the solvent was distilled under reduced pressure and then purified by column chromatography (EtOAc: CH_2Cl_2 =2:1, 1.2 g, 80%). ^1H NMR (400 MHz, CDCl_3): δ 6.25 (s, 2H), 4.69 (s, 2H), 4.35 (s, 4H), 4.22 (s, 10H), 3.69 (s, 4H), 3.66 (t, $J = 4.6$ Hz, 4H), 3.63 - 3.55 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ 170.54, 71.42 70.47, 70.26, 68.99, 39.26. FTIR: 3313(-NH), 3103(Ar-C-H), 2984-2790(- CH_2 -), 1623(C=O), 1107(C-O). LC-MS(ESI+) m/z calculated for $\text{C}_{28}\text{H}_{32}\text{Fe}_2\text{N}_2\text{O}_4$ ($\text{M}+\text{Na}$) $^+$ 575, observed 574.70.



Scheme S2 Synthesis of 1,8-diamino-3,6-dioxaoctane bridged bis(ferrocene)

General preparation of supramolecular polymer nanoparticles via host-guest interaction. A solution of PHEAm-β-CD (8 mL, 1.25 mg/mL) in H_2O was stirred vigorously with slow addition of BisFc (2 mL, 0.335 mg/mL) in EtOH over 30 min. The solution was then stirred for another 3 h.

S.3 Characterization

^1H NMR and ^{13}C NMR measurements were carried out on a Bruker AMX 300 spectrometer, CDCl_3 , D_2O , and d_6 -DMSO as the

solvents. FTIR analysis of the samples was carried out on a thermo Bruker EQUINOXSS/HYPERION2000 spectrometer. Mass measurement was performed on a Shimadzu Prominence-LCMS 2020 Equipped with a SPD-20A photodetector (200-800 nm) and an MS spectrometer (MS 2020; m/z range: 10-2000; ionization modes: ESI+). UV/Vis spectra were recorded on a Mapada UV-6300 spectrophotometer (Shanghai Mapada Instruments Co. Ltd.). Gel permeation chromatography (GPC) was carried out on Waters Binary HPLC system using H₂O containing 0.8 wt% NaNO₃ as the eluent. The molecular weight of the polymers was calculated relative to linear poly(ethylene oxide) standard. The controlled assembly and disassembly of single-chain nanoparticles were conducted via a potentiostat with a bare platinum disk electrode as a working electrode and a platinum wire as a counter electrode in a glass electrochemical cell at room temperature. TEM of the sample was performed on Hitachi H-600, operating with an acceleration voltage of 150 KV. TEM samples were prepared by placing one drop of nanoparticles solution (c=0.2 mg/mL) on a 200 mesh carbon-coated copper grid and left in air to dry. The average size of the nanoparticles was also determined on DLS (Malvern Autosizer 4700), equipped with a solid-state laser (ILT 5500QSL, output power 100 mW at $\lambda=532$ nm) as light source. The solution was filtered through a 0.45 μ m filter before the measurement. The height and size distribution of the nanoparticles were determined by tapping-mode AFM (SPA-300HV, Seiko Instruments Inc.). The standard silicon tips were used. All samples were prepared by drop-casting 10 μ L of nanoparticles solution (c=10 μ g/mL) on silicon wafer with drying at ambient temperature.

S.4 Supplementary Data

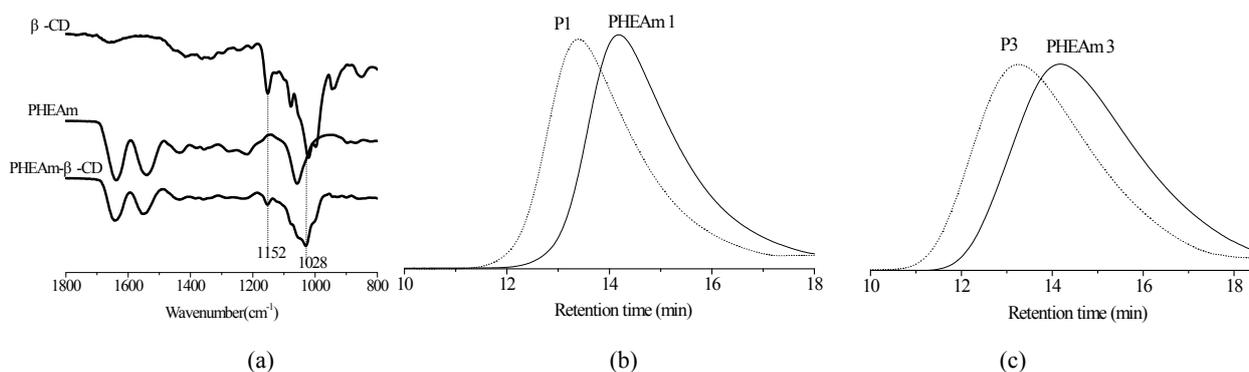


Fig. S1 (a) FTIR of β -CD, PHEAm, and PHEAm- β -CD; (b) and (c) are GPC curves of PHEAm precursors and the corresponding PHEAm- β -CD (P1 and P3).

Table S1 GPC data of PHEAm precursors.

Precursors	Mn ^a	PDI ^a
PHEAm 1	36500	1.24

PHEAm 2	27400	1.28
PHEAm 3	39700	1.40

a Determined by GPC, using H₂O (containing 0.8 wt% NaNO₃) as eluent.

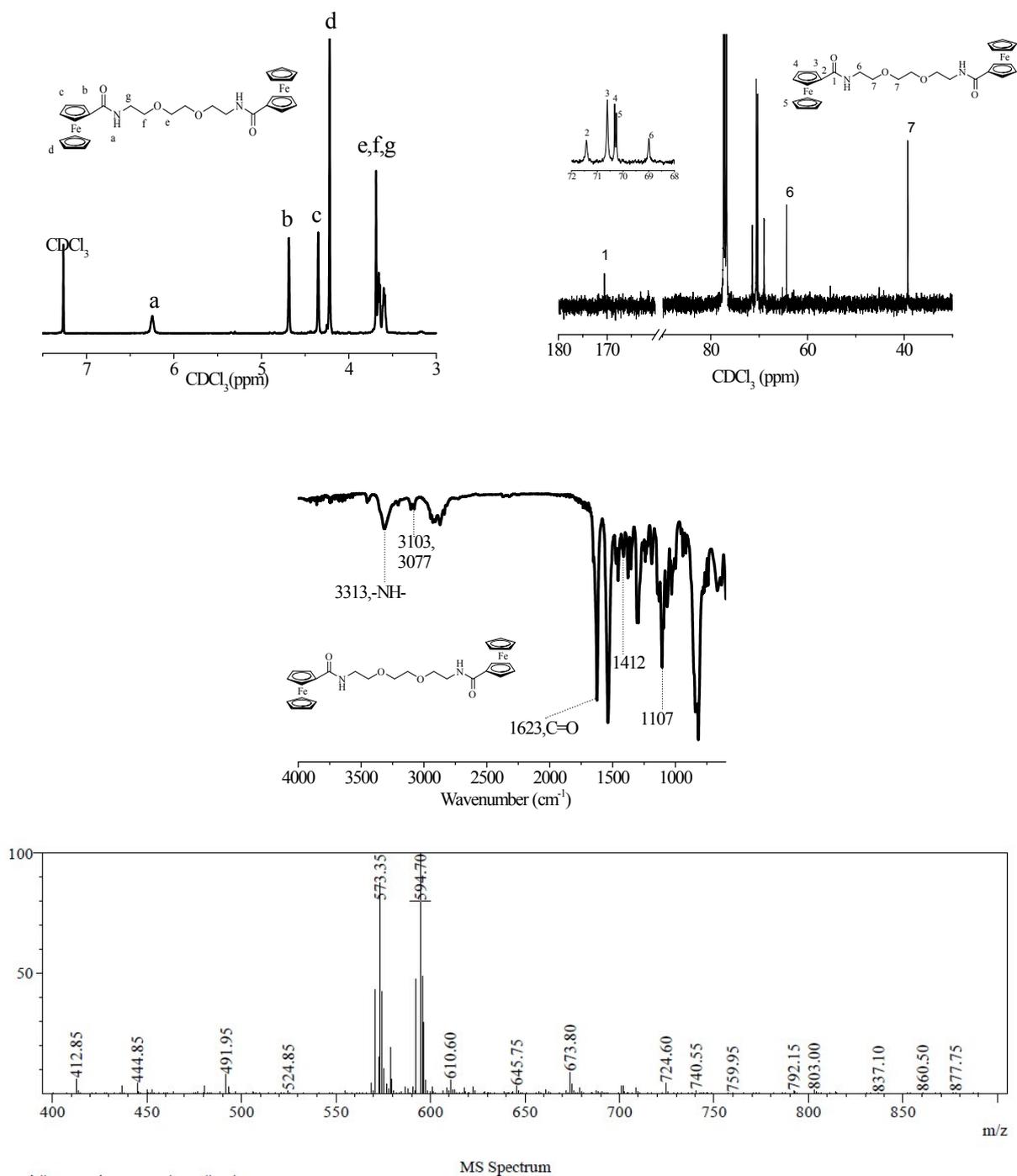


Fig. S2 ¹H NMR, ¹³C NMR, FTIR, and MS spectrum of 1,8-diamino-3,6-dioxaoctane bridged bis(ferrocene).

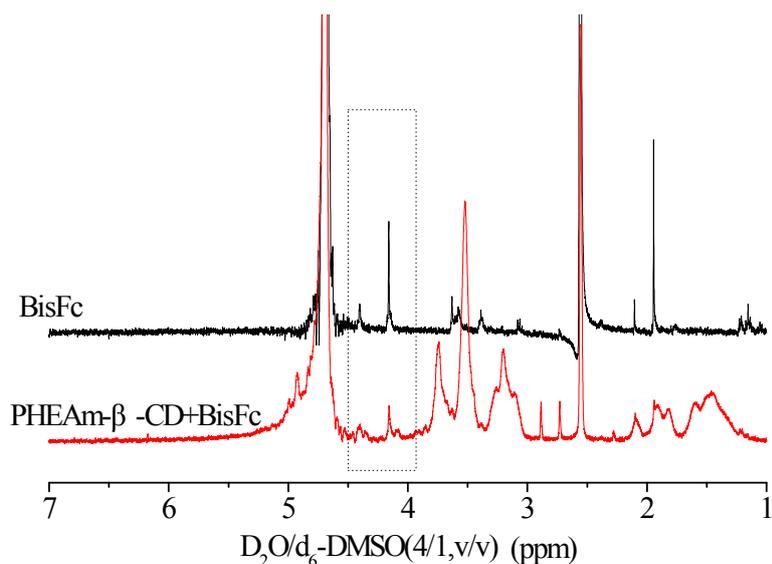


Fig. S3 Overlay of Figure 3b (Both samples were scanned for 64 times)

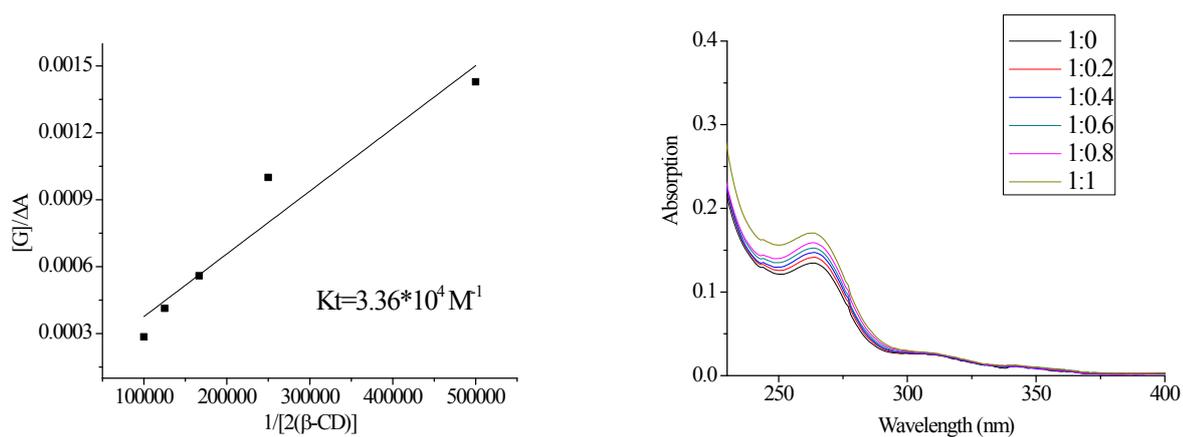
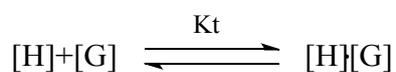


Fig. S4 (a) The UV absorption of BisFc upon stepwise addition of β -CD, the concentration of BisFc keeps 1×10^{-5} M; (b) UV/Vis spectra of BisFc (1×10^{-5} M) and 2β -CD at different molar ratios from 10:2 to 1:1.

The bonding affinity of β -CD with 1,8- diamino-3,6-dioxaoctane bridged bis(ferrocene) in $H_2O/EtOH$ was determined via UV/Vis measurement which is similar to the literature.² The absorption at 263 nm in UV/Vis spectra is the characteristic absorption of Fc species. The concentration of BisFc was kept at 1×10^{-5} M. The absorption of binary mixture increased with gradual addition of the β -CD into BisFc solution. The inclusion complexation of BisFc/ 2β -CD is expressed by the following equation:



Hidebrand-Benesi equation was employed here:

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

Where H, G, Kt represent as host β -CD, guest BisFc, and association constant respectively. ΔA denotes the absorbance difference before and after addition of β -CD. $\Delta\epsilon$ denotes the difference of the molar extinction coefficient between the host and host-guest complex at the same wavelength and is $1.06 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ in this work. The association constant Kt calculated by the equation is $3.36 \times 10^4 \text{ M}^{-1}$.

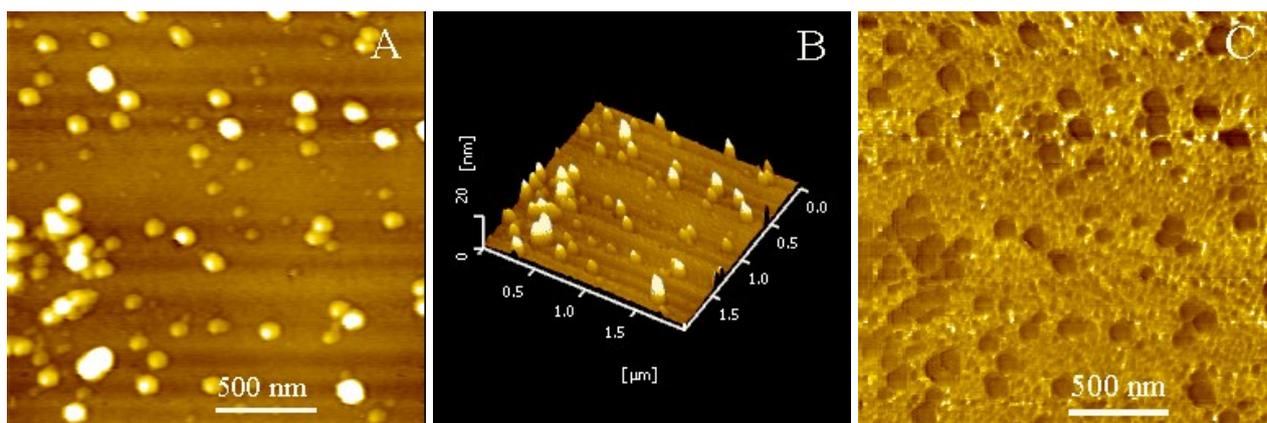


Fig. S5 AFM images of PHEAm- β -CD ($c=10 \mu\text{g/mL}$, $10 \mu\text{L}$) drop-cast onto silica wafer: A, top-view; B, 3D image; C, phase image.

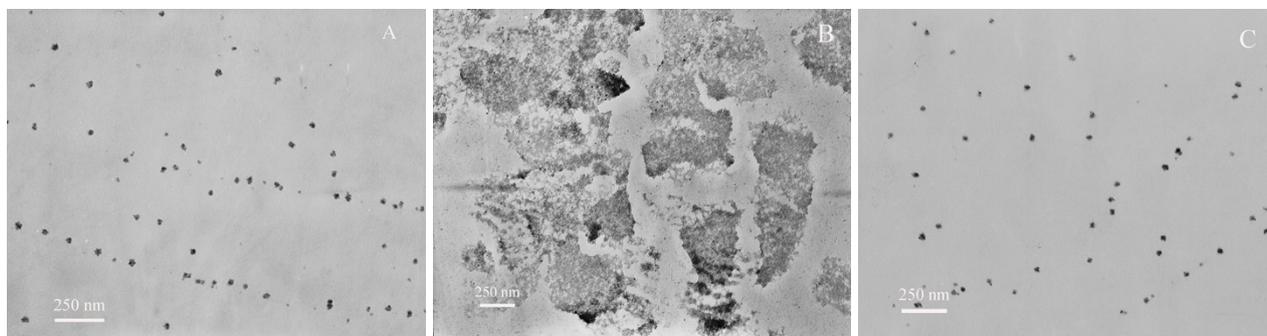


Fig. S6 TEM images of the reversible collapsing and discollapsing of the voltage-responsive single-chain nanoparticles upon electric stimuli: A, no external stimuli; B, +1.5 V, 3 h, in some area of the carbon-coated copper grid, polymer film formed; C, -1.5 V, 3 h.

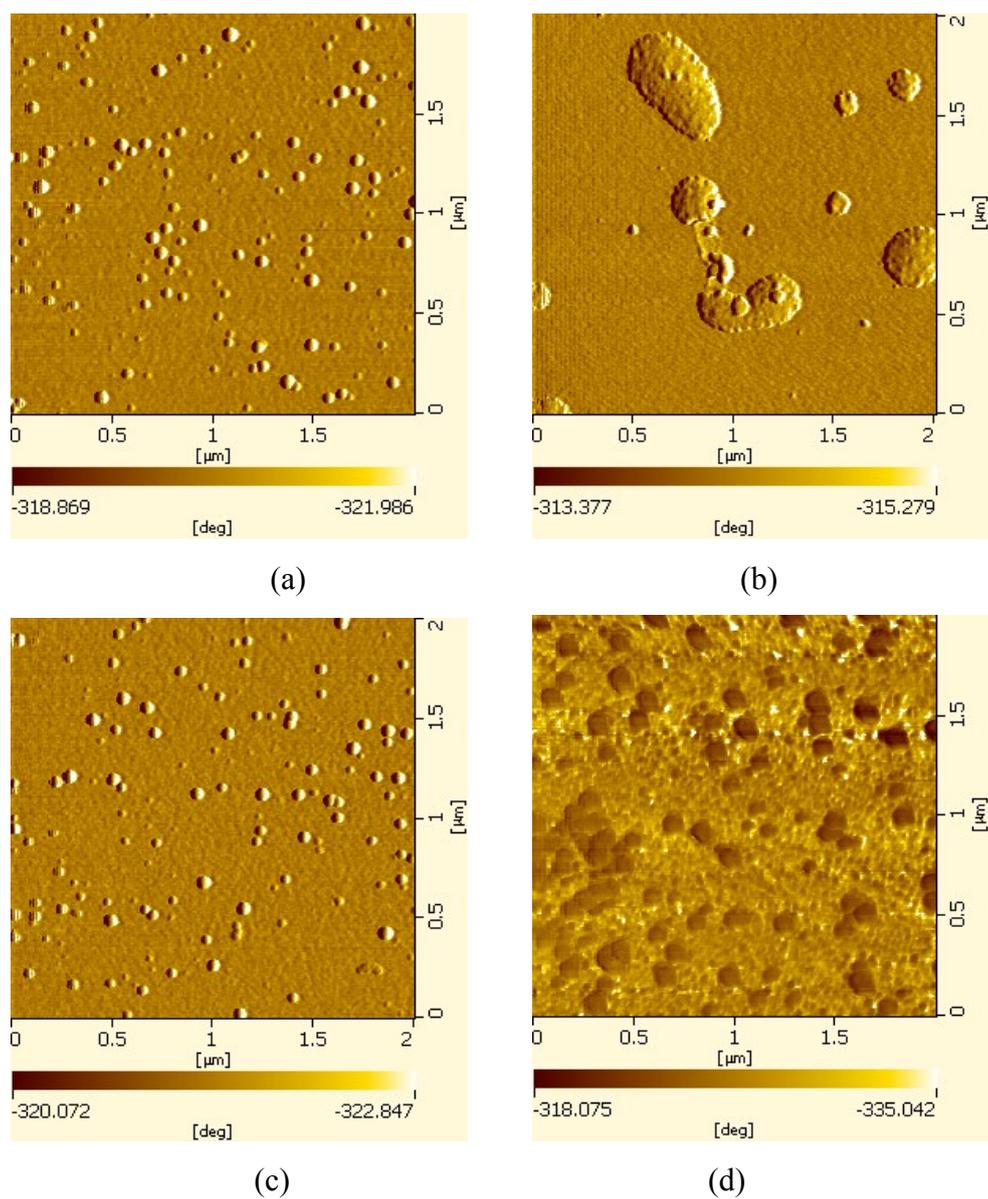


Fig. S7 AFM phase images of (a) nanoparticles; (b) upon +1.5 V voltage stimuli; (c) upon -1.5 V voltage stimuli and (d) PHEAm- β -CD. Clear difference between nanoparticles and linear polymer in the solid state can be seen through AFM phase images.

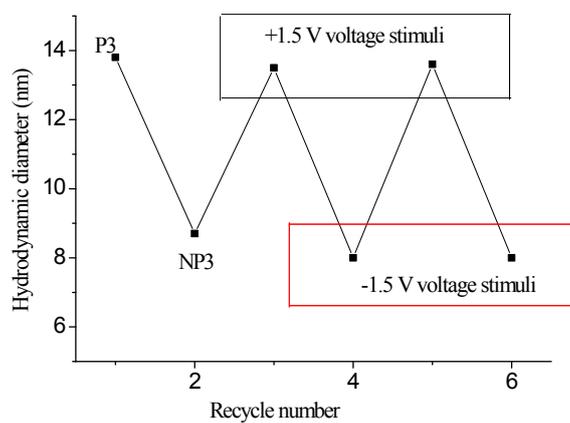


Fig. S8 DLS results of intramolecular assembly and disassembly of supramolecular nanoparticles (NP3) via voltage-stimuli

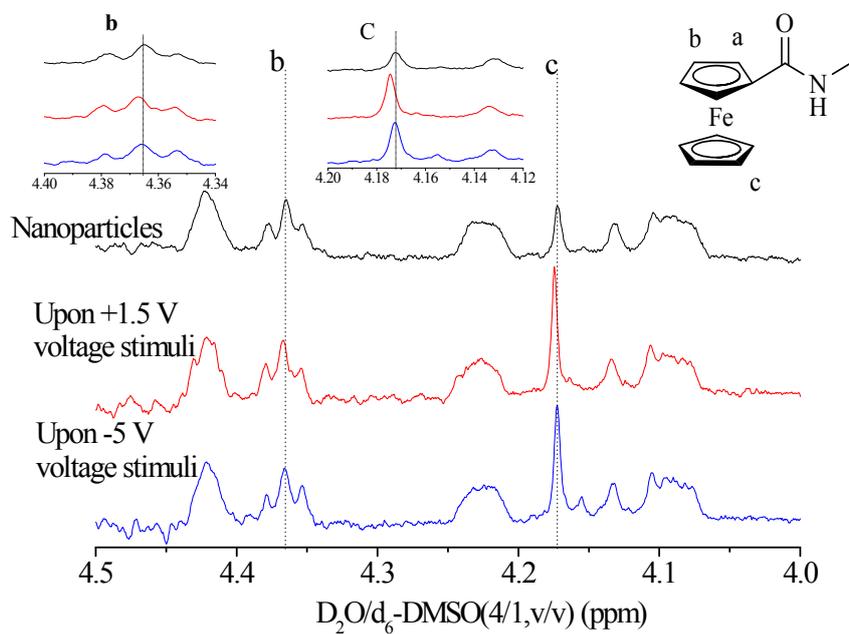


Fig. S9 ¹H NMR of nanoparticles(NP2) before voltage stimuli(black), upon +1.5 V voltage stimuli (red line) and upon -1.5 V voltage stimuli (blue line). (all samples were scanned for 256 times)

Notes and references

- (a) R.C. Petter, J.S. Salek, C.T. Sikorski, G. Kumaravel, F.T. Lin, *J. Am. Chem. Soc.*, 1990, **112**, 3860; (b) M.H. Stenzel, T.P. Davis, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 4498.
- L. Peng, A. Feng, H. Zhang, H. Wang, C. Jian, B. Liu, W. Gao, J. Yuan, *Polym. Chem.*, 2014, **5**, 1751.