Supporting Information

Dual Stimuli-Responsive Nano-Structures Transition of Three-Arm Branched Amphiphilic Polymers Containing Ferrocene (Fc) and Azobenzene (Azo) Moieties in Aqueous Solution

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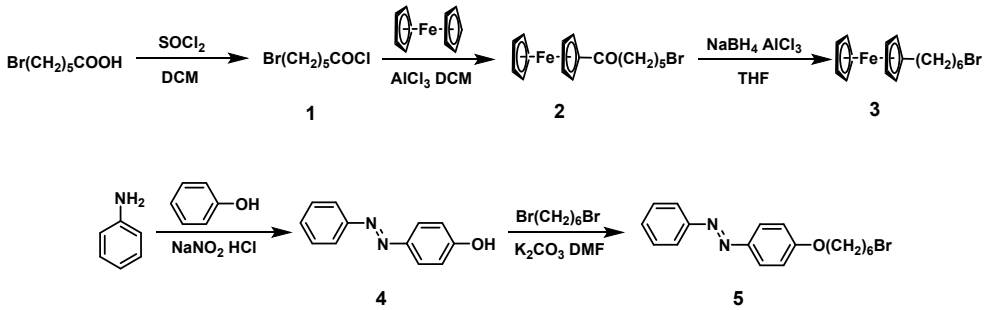
Syntheses of 6-Bromoundecyl Ferrocene (3)

6-Bromoundecyl ferrocene was synthesized according to our previous works and the synthetic route was shown in Scheme S1. Briefly, 6-bromohexanoic acid was dissolved in DCM, and then $SOCl_2$ was added dropwise under an argon atmosphere. The mixture was refluxed for 4 h under stirring. The resultant solution was concentrated in vacuum obtained **1**. Product **1** was dissolved in DCM again and added dropwise into a mixture of ferrocene and $AlCl_3$ in DCM for about 1 h under argon. After stirring overnight, the solution was poured into NaCl saturated ice-water, and the organic layer was extracted with DCM, washed twice with water, and concentrated. The resultant solid was purified by column chromatography to yield **2**. After that, compound **2** in dry THF was slowly added into a stirred suspension of $NaBH_4$ and $AlCl_3$ in dry THF under an argon atmosphere. After stirring for 3 h at room temperature, water was added to the resultant mixture, and the organic layer was extracted with ethyl acetate, washed twice with water, and concentrated. The residue was purified by column chromatography to yield 6-bromoundecyl ferrocene (**3**). ^{1}H NMR ($CDCl_3$, TMS) δ (ppm): 1.31 (m, 6H, -(C*H*$_2$)$_3$-), 1.86 (m, 2H, -C*H*$_2$-CH$_2$-Br), 2.24 (t, 2H, -C*H*$_2$-Cp), 3.41 (t, 2H, -C*H*$_2$-Br), 4.31 (m, 9H, *H*(Cp)).

Syntheses of 6-Bromohexyloxy Azobenzene (5)

The synthetic route is shown in Scheme S1 also. First, compound **4** was synthesized according to the reported method. After that, an excess amount of 1,6-dibromohexane in acetone with dry potassium carbonate was added to **4**. The reaction mixture was allowed to react for 12 h at 55°C and then extracted with methylene dichloride, purified by silica gel column chromatography to yield **5**. ^{1}H NMR ($CDCl_3$, TMS) δ (ppm): 1.35 (m, 4H, -(C*H*$_2$)$_2$-), 1.79 (m, 4H, -C*H*$_2$-CH$_2$-Br, -C*H*$_2$-CH$_2$-O-Ar), 3.52 (t, 2H, -C*H*$_2$-Br), 4.06 (t, 2H, -C*H*$_2$- O-Ar), 7.00 (d, 2H, *H*(Ar)), 7.43 (t, 1H, *H*(Ar)), 7.50 (t, 2H, *H*(Ar)), 7.90 (q, 4H, *H*(Ar)).

Scheme S1 Synthetic Routes of 6-Bromoundecyl Ferrocene (3) and 6-Bromohexyloxy Azobenzene (5)



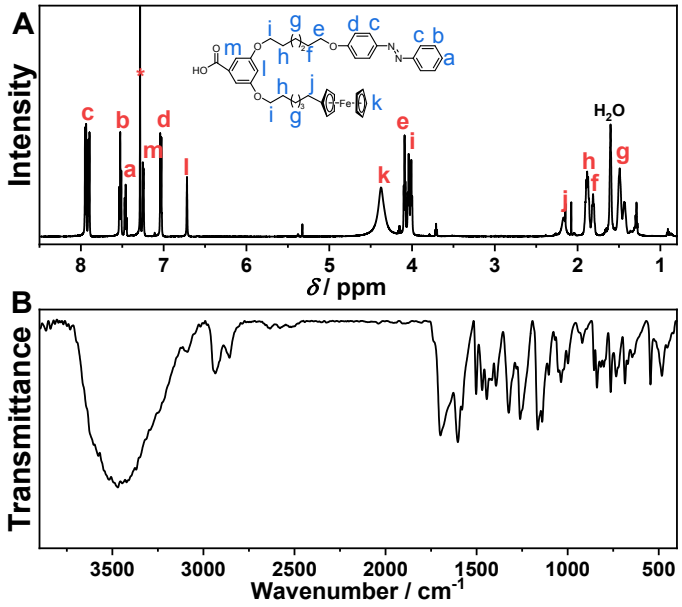


Fig. S1 (A) ^{1}H NMR and (B) FT-IR spectra of Perce-type mini-dendron 3-(6-ferrocenyhexyloxyl)-5-(6-azobenzenehexyloxy) benzoic acid.

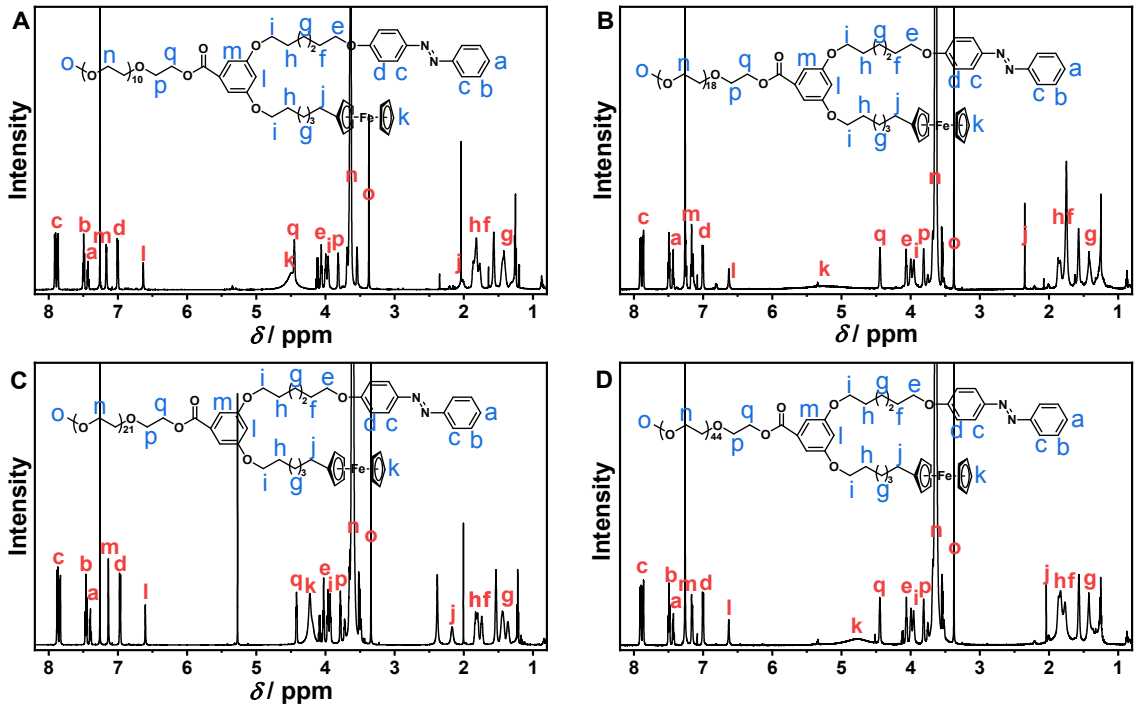


Fig. S2 ^{1}H NMR spectra of the AzoFcPEO amphiphilic polymers.

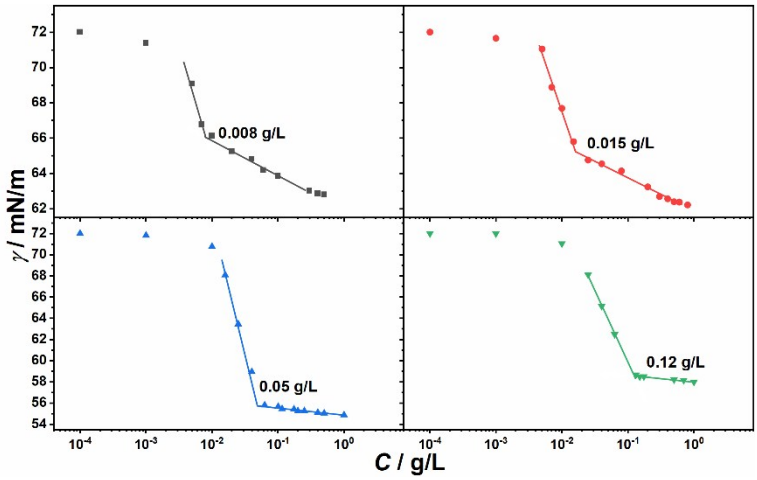


Fig. S3 Plots of surface tensions against the concentration of AzoFcPEO$_{11}$ aqueous solution upon exposure to different stimuli.

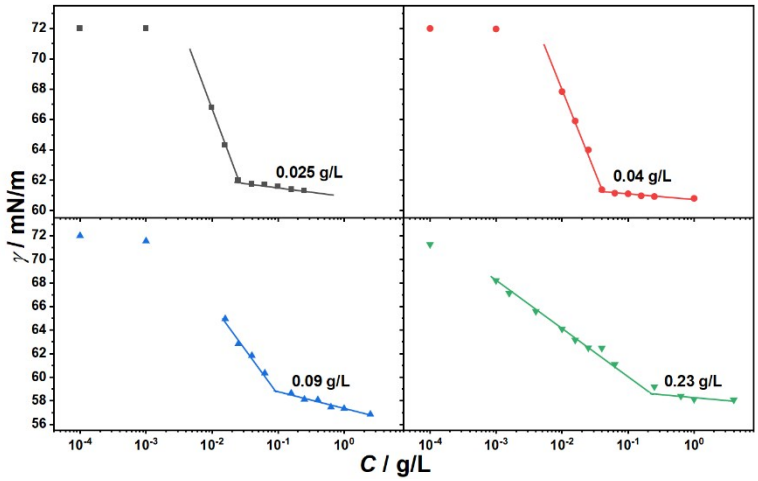


Fig. S4 Plots of surface tensions against the concentration of AzoFcPEO$_{19}$ aqueous solution upon exposure to different stimuli.

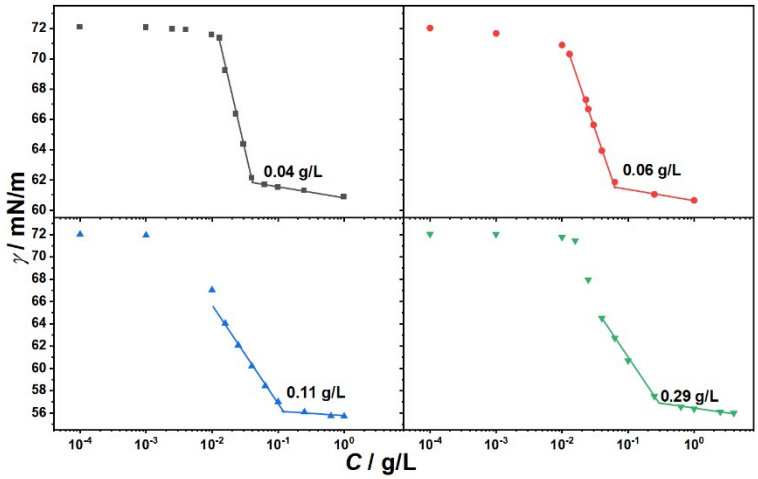


Fig. S5 Plots of surface tensions against the concentration of AzoFcPEO$_{22}$ aqueous solution upon exposure to different stimuli.

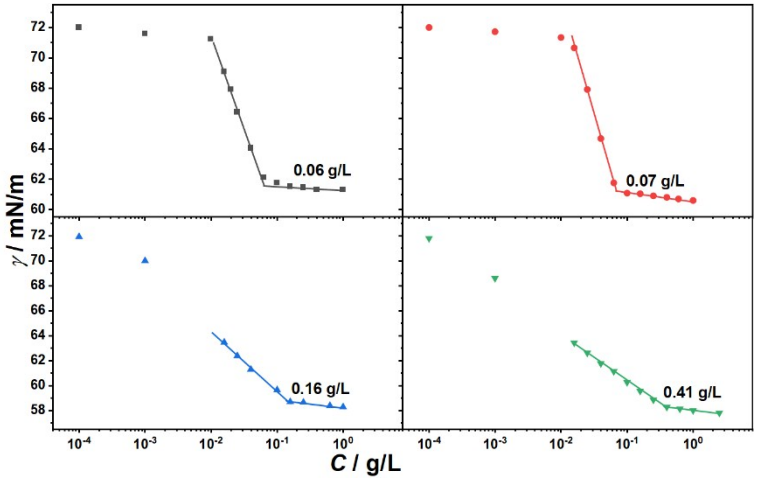


Fig. S6 Plots of surface tensions against the concentration of AzoFcPEO$_{45}$ aqueous solution upon exposure to different stimuli.

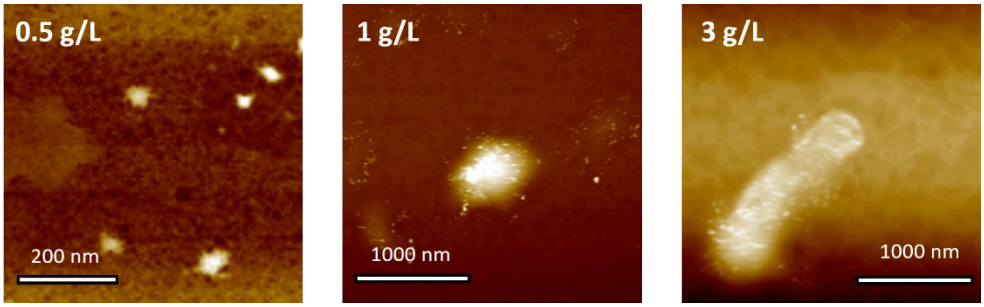


Fig. S7 AFM images of CMs of AzoFcPEO$_{11}$ solution at indicate concentration.

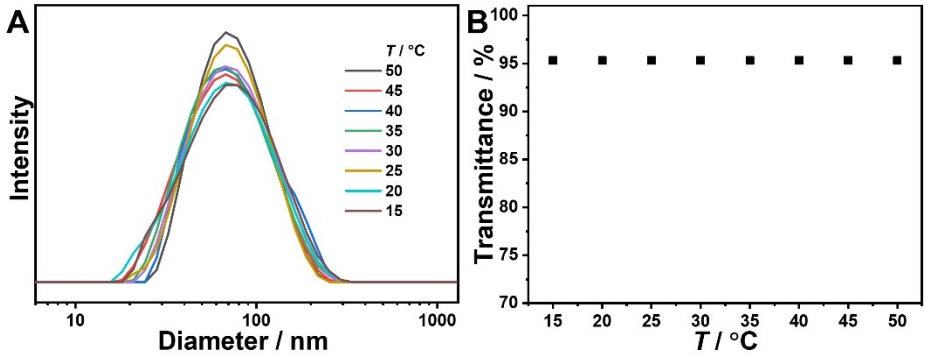


Fig. S8 DLS and transmittance measurements of AzoFcPEO$_{16}$ solution (0.5 g/L) at different temperature.

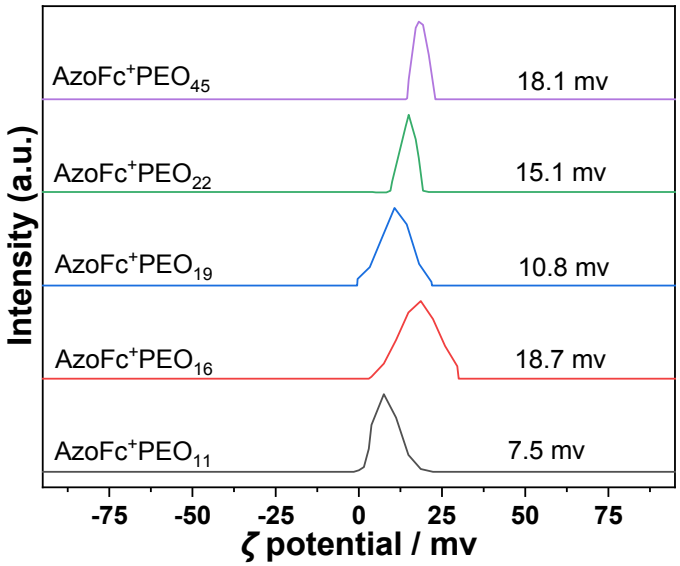


Fig. S9 Zeta potential of the AzoFc⁺PEO amphiphilic polymers.

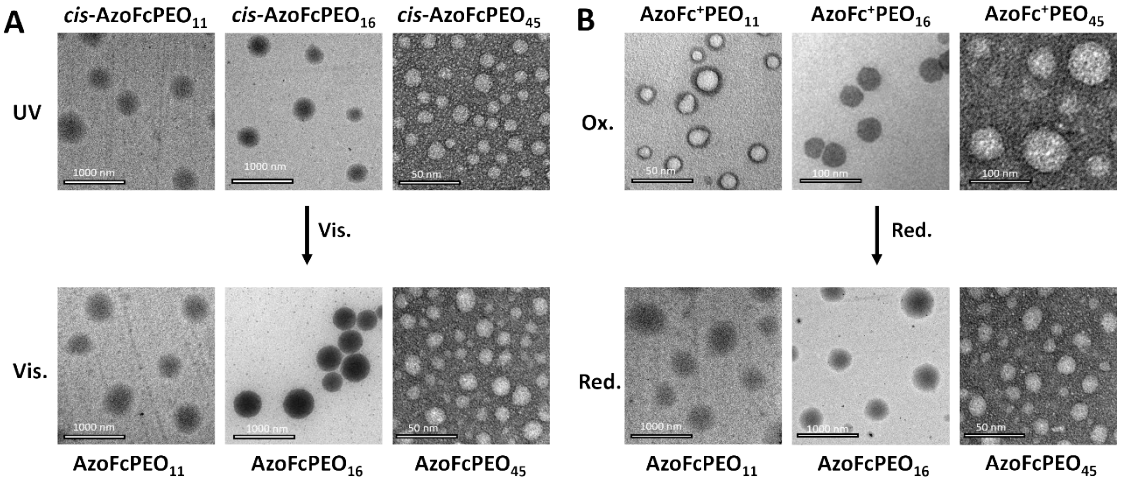


Fig. S10 Reversible nanostructures transition of the AzoFcPEO amphiphilic polymer solution upon exposure to visible light (A) or reducer VC (B).