Voltage-responsive reversible self-assembly and controlled drug

release of ferrocene-containing polymeric superamphiphile

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Synthesis of block copolymers PEG$_{113}$-*b*-PAA$_{30}$
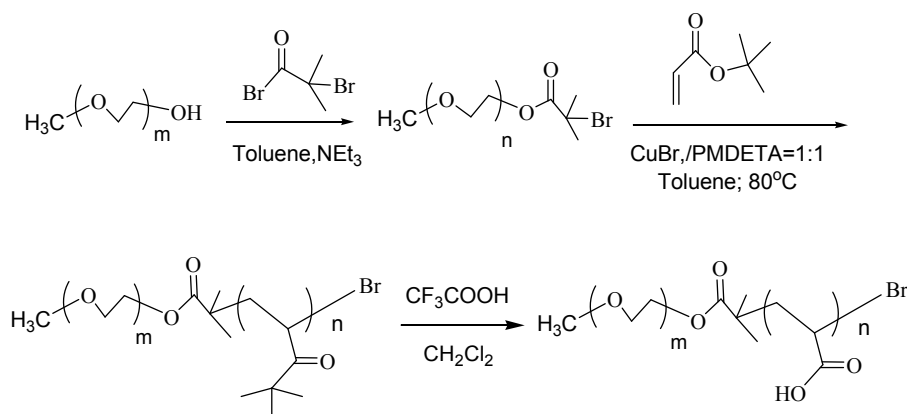
Scheme S1   Synthetic route of PEG$_{113}$-*b*-PAA$_{30}$

The block copolymer PEG$_{113}$-*b*-PAA$_{30}$ was synthesized by atom transfer radical polymerization (ATRP), which were performed on a self-made fask that consisted of two 20 mL round-bottomed fasks joined through a glass tube with about 6 mm in inner diameter (Scheme S1).[1, 2] The PEG macroinitiator (CH$_3$O-PEO-Br) was synthesized through quantitative esterification of 2-bromoisobutyryl bromide with poly(ethylene glycol) methyl ether (CH$_3$O-PEO-OH, Flakes) as described in the literatures.[3] Tert-butyl acrylate (TBAA), CH3-PEG-Br (0.15 mmol), CuBr (22mg, 0.15 mmol), and a magnetic stirrer were loaded into one of the two fasks, while *N,N,N',N'',N''*-penta-methyl diethylenetriamine (PMDETA) (27 mg, 0.15 mmol) and toluene (10 mL) were added into the other fask. The liquid mixture was degassed through three freeze-pump-thaw cycles to remove trace of oxygen and backfilled with argon before it was added to the other fask. After 10 min stirred to dissolve CuBr at room temperature, the reaction mixture was stirred in the preheated 80 ˚C oil bath for 24 h. The reaction was stopped by rapid cooling in liquid nitrogen and exposing the mixture to air. The blue reaction mixture was passed though a short silica gel column to remove copper complex, and was precipitated in 50 mL of hexane to yield 1.20g (77.9 wt %) of PEG-*b*-P*t*BA.

In Fig. S1, two signals at 3.65 and 3.38 ppm are due to the methylene protons (–OCH$_2$CH$_2$O–) and the methyl protons (-OCH$_3$) of PEO block, respectively, and the resonance at 1.43 ppm corresponds to the tert-butyl protons (–C(CH$_3$)$_3$) in the P*t*BA block. The polymerization degree of the P*t*BA block (DP$_{tBA}$) was estimated as DP$_{tBA}$ =($I_{1.43}$/9)/($I_{3.38}$/3), where $I_{1.43}$ and $I_{3.38}$ were the NMR peak areas at 1.43 ppm for the tert-butyl group and at 3.38 ppm for the PEO methyl group, respectively.

Trifluoroacetic acid (CF$_3$COOH, 5-fold excess of the t-butyl group in mole) was added into a dichloromethane (CH2Cl2) solution of PEG$_{113}$-b-PtBA$_{30}$ (1.00 g) at 0°C under vigorous stirring. The reaction was kept at 0 °C for 3 h and then at room temperature for 24 h. The solvent and residual CF$_3$COOH were removed by evaporation. The

product was washed several times with ether to remove trace of CF_3COOH thoroughly and then filtered and dried in vacuum at room temperature. The resulting white powder was PEG$_{113}$-b-PAA$_{30}$ (0.73 g, 90% yield). NMR results demonstrated that the PtBA block was successfully converted to PAA (Fig. S2).

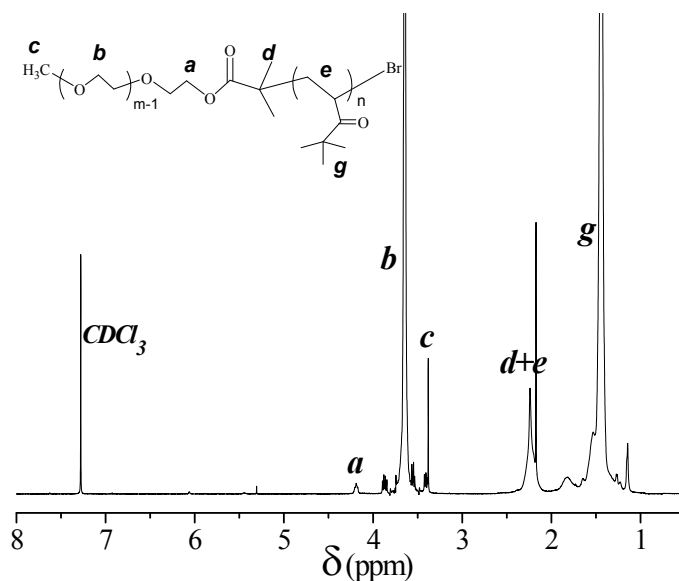**Fig. S1** ^{1}H NMR spectra of PEG-b-PtBA measured in CDCl$_3$.

Table S1 Characterization of PEO-Br and PEG-b-PtBA

Sample	M_n [a]	M_w [a]	M_w/M_n [a]	$M_{n, NMR}$ [b]	DP [b]
CH$_3$O-PEG$_{113}$-Br	5400	5800	1.07	5149	
PEG$_{113}$-b-PtBA$_{30}$	9300	10500	1.13	8994	30

[a]: Determined by GPC in THF at 1.0 mL/min using PS standard.

[b]: Determined by ^{1}H NMR.

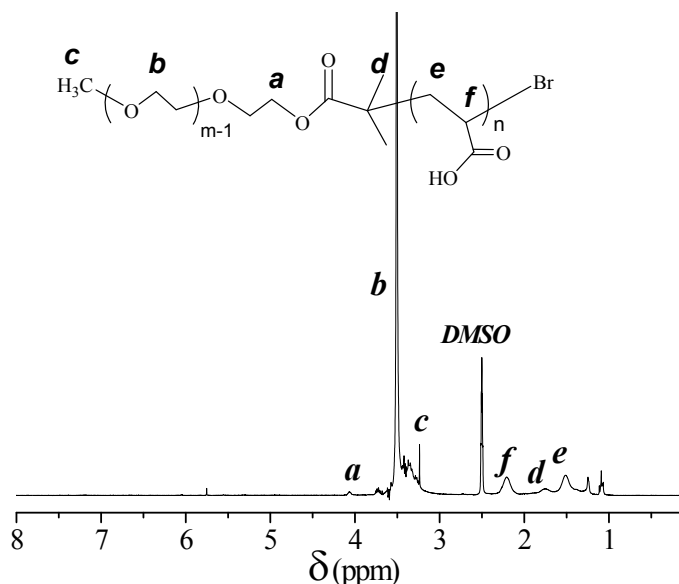**Fig. S2** ^{1}H NMR spectra of PEG$_{113}$-b-PAA$_{30}$ measured in DMSO.

Electrochemical redox rate of polymeric superamphiphile PEG$_{113}$-b-PAA$_{30}$/FTMA in solution

In order to find the optimum redox potential, amperometric i-t curves under different redox voltage were

tested (Fig. S3). As shown in Fig. S3A, under the certain oxidation voltage, oxidation current drops rapidly in several seconds after reaction, which should be the charging phenomenon of electric double layer formed on the electrode surface. And then oxidation current is slow down with the increase of the reaction time, which is because the concentration of ferrocene groups in the reduction state decreases gradually in the solution. These amperometric *i-t* curves can be described by the equation 1 which was deduced by Cottrell equation[4].

$$i(t) = \frac{nFAD^{1/2}c_0}{(\pi t)^{1/2}} + i_1$$

(1)

where *i(t)* is the reaction current when the electrochemical reaction time is *t*, *n* is the electronic transference number of electrochemical reactions, *F* is Faraday constant, *A* is area of the planar electrode, *D* is diffusion coefficient for complexes, c_0 is the initial concentration of the ferrocenyl groups, *t* is the reaction time, and i_1 is the double-layered capacitance charging current.

In order to tune electrochemical redox rates, the variation curves of oxidation or reduction degree *P* against the redox time *t* for ferrocenyl groups were also tested, as shown in Figure 2. When the electrochemical reaction time is *m*, the oxidation or reduction degree *P* of ferrocene groups can be calculated by equation 2.

$$P = \frac{\int_0^m idt}{C_0 V_0 nF} \times 100\%$$

(2)

where *m* is the electrochemical reaction time, *i* is the reaction current, C_0 is the initial concentration of the ferrocenyl groups, V_0 is the initial volume of the complex aqueous solution, *n* is the electronic transference number of electrochemical reactions, and *F* is Faraday constant.

In a certain voltage range (+0.30 to +1.00 V), with the increase of oxidation potential, the oxidation current of complex solution also increase, and the oxidation time (when ferrocene groups is completely oxidized) reduces from 3.8 h to 0.7 h. In addition, in a certain voltage range (+0.05 to -0.20 V), with the decrease of reduction potential, the reduction current increase also (Fig. S3C), and the reduction time (when ferrocene groups is completely reduced) reduces from 1.8 h to 0.3 h (Fig. S3D).
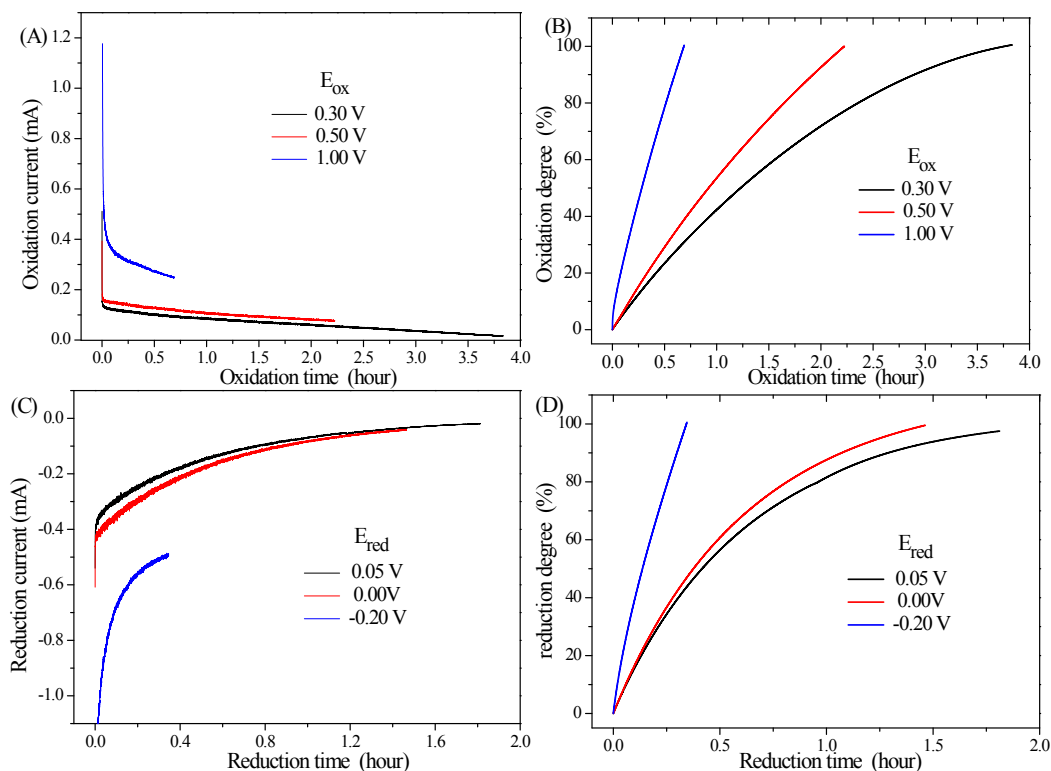

Fig. S3 Amperometric *i-t* curves and Plots of redox degree against the redox time for PEG$_{113}$-*b*-PAA$_{30}$/FTMA in 0.10 M NaCl aqueous solution at different redox potentials. The concentration of polymeric superamphiphile (Z=1:1) is 0.40 mg/mL.
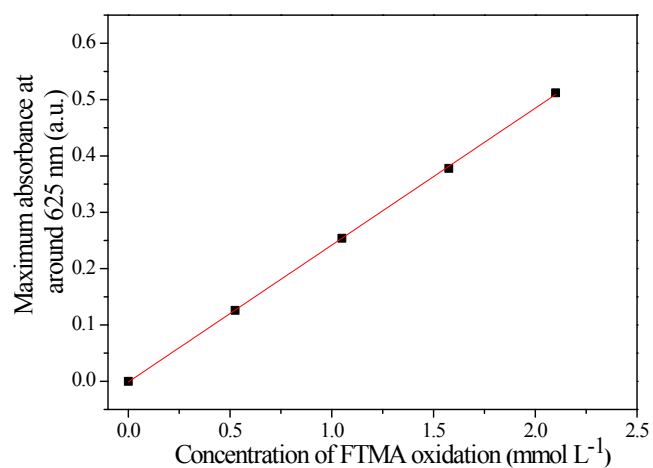
Fig. S4 The absorption intensity of FTMA in the oxidation state at 627 nm at different concentrations in aqueous solutions.
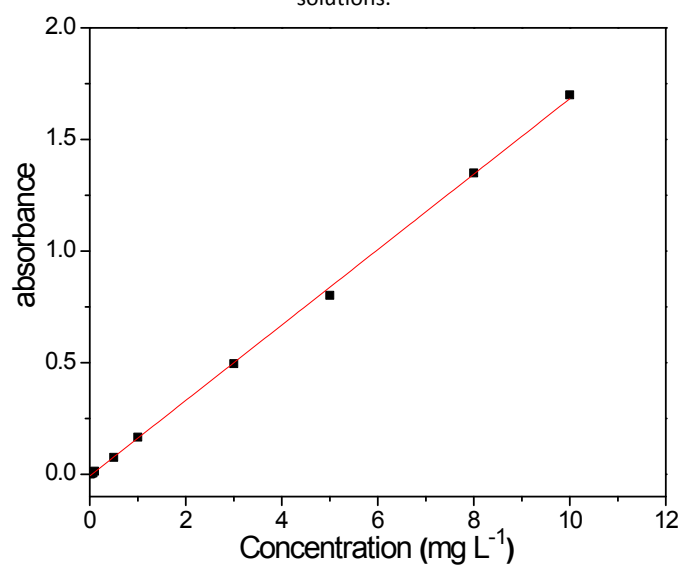

Fig. S5 The absorption intensity of R6G at 527 nm in different concentration aqueous solutions.

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