Supporting Information

UV and pH-responsive supra-amphiphile driven by combined interactions for controlled self-assembly behaviors

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Synthesis of (E)-4-(phenyldiazenyl) phenyl 4-formylbenzoate (PPB)

As shown in figure S1, 4-hydroxyl azobenzene was synthesized as follows: phenylamine (1.86 g, 20 mmol) was dissolved in 25 ml water and concentrated hydrochloric acid (HCl, 12 mol/L, 5 mL) was added at 0°C. A solution of sodium nitrite (1.49 g, 21 mmol) in water (20 mL) was added dropwise while the temperature was maintained below 5°C. After stirring for 20 min, a solution of benzenediazonium chlorides was prepared. Subsequently, the solution was added gradually into a mixture of phenols (1.88 g, 20 mmol), sodium hydroxide (NaOH, 20 mmol), ethanol (15 mL) and water (25 mL) at 0-5°C. The mixture was continued to stir for 3-6 h until
a lot of precipitate was produced. The solid was filtered, washed with water (3 × 20 mL) and used without purification.

A solution of 4-formylbenzoic acid (0.31g, 2mmol), DCC (0.45g, 2.2 mmol), DMAP (0.20g, 2mmol) in 50ml DCM was stirred for 2h at room temperature. Then 4-hydroxy azobenzene (0.396g, 2mmol) was added and the reaction continued for 48h. The resulting precipitate was filtered and the DCM was evaporated on a rotavapor. The product was washed with hydrochloric acid and water, purified by column chromatography (silica gel, PE and EA as eluent) gave orange solid to yield 37%. ¹H NMR (300 MHz, CDCl₃), δ: 10.16 (s, 1H), 8.40 (d, 2H), 8.06-8.02 (dd, 4H), 7.94-7.92 (d, 2H), 7.55-7.49 (m, 3H), 7.42 (d, 2H). m/z: 331.11.

Fig. S2 ¹H NMR spectra of (E)-4-(phenyldiazenyl) phenyl 4-formylbenzoate.
Fig. S3 UV-vis spectra of PPB in (a) DMSO and in aqueous solution; (b) in THF and in aqueous solution.

Fig. S4 UV/vis spectra of α-CD/PPBI (Host/Guest = 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1) for Job’s plots in water at room temperature.
Fig. S5 Time-dependent UV-vis spectra of PPB.

Fig. S6 $^1$H NMR spectra from the same tube of $\alpha$-CD/PPBI before and after UV irradiation (400 MHz in D$_2$O at 298 K, 365 nm, 30 min).
Fig. S7 TEM images of vesicles loaded with RHB