Supporting Information

Smart Azobenzene-Containing Tubular Polymersomes: Fabrication and Multiple Morphological Tuning

Lishan Li, ¹ Songbo Cui, ³ An Hu,¹ Wei Zhang,¹ Yiwen Li,*,² Nianchen Zhou,*,¹ Zhengbiao Zhang ¹ and Xiulin Zhu¹

1. State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, P. R. China.

2. College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, P. R. China.

3. Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo N2L 3G1, Ontario, Canada.

*Email: <u>nczhou@suda.edu.cn</u>; ywli@scu.edu.cn.

EXPERIMENTAL SECTION

Materials

Poly (ethylene glycol) mono methyl ether with a number-average molecular weight of about 5000 was obtained from meryer and was purified by azeotropic distillation with toluene before use. Copper(I) bromide (CuBr; chemical pure; Shanghai Chemical Reagent, Shanghai, China) was first washed with excess acetic acid, followed by ethanol and ether, and it was then dried. N, N, N', N'', N''-Pentamethyldiethylenetriamine (PMDETA; 98%; Jiangsu Liyang Jiangdian Chemical Factory, China) was distilled three times under reduced pressure. 1,4-Dioxane was purchased from Sinopharm Chemical Reagent Co., Ltd. and was dried over CaH₂ and distilled before use. Carboxyfluorescein (\geq 97%; Energy), hydrazine hydrate(85%; Sinopharm Chemical Reagent Co., Ltd.) 2,6-difluoroaniline (\geq 97%; Aladdin), 3,5difluorophenol (\geq 98%; Accela), aniline (\geq 99%; Alfa), phenol (\geq 99%; Alfa), 4aminobenzonitrile (\geq 98%; Tci), 6-bromo-1-hexanol (\geq 98%; Aldrich), methylacryloyl chloride (Analytical grade; Shanghai Chemical Reagent, Shanghai, China) were used as received. All the others not listed here are used as received.

Synthesis

Synthesis of 2, 6, 2', 6'-tetrafluoro-(4-hydroxy) azobenzene (FAzoOH)

2, 6-difluoroaniline (12.90 g, 0.1 mol) were dissolved in 30 mL of concentrated hydrochloric acid and 30 mL of water was added. The resulting solution was stirred for half an hour at room temperature and then cooled to 0 °C. To this cooled solution, sodium nitrite (7.59 g, 0.11 mol) dissolved in 100 mL cooled deionized water was slowly added by maintaining the temperature in the range 0 to 5 °C. After a clear solution of the diazonium salt was formed, the resulting mixture was stirred for half an hour and slowly added to 3,5-difluorophenol (13.01 g, 0.01 mol) in sodium hydroxidesolution (10 g, 0.25 mol in 250 mL water) at 0 °C. In the progress during adding the solution of diazonium salt, the pH of the mixture solution was vigorously stirred at 0 °C for 1 h, then stirred for 12 h at room temperature and hydrochloric acid aqueous solution (1 N) was added to adjust the pH to 5 to 7. The solution was kept for 10 min, and then the precipitated product was purified by column chromatography (silica gel, EtOAc). (14.85 g, yield: 55%). ¹H NMR (300 MHz, CDCl₃, δ), (TMS, ppm): 6.53 (2H, ArH), 7.03 (2H, ArH), 7.31(1H, ArH).

Synthesis of 2, 6, 2', 6'-tetrafluoro-(4-(6-hydroxyhexyloxy)) azobenzene (FAzoC₆OH)

To 8.48 g of FAzo (31.4 mmol) in 500 mL of dried DMF was added 20 g of anhydrous potassium carbonate and 0.5 g of potassium iodide. The resulting mixture was stirred for half an hour at 70 °C. Then 5 mL of 6-bromo-1-hexanol (38 mmol) was added drop-wise and the stirring was continued. The completion of the reaction was checked by thin layer chromatography using ethyl acetate as eluant. The reaction was continued for 24 h. After cooling to room temperature, the reaction mixture was filtered and the solution was distilled under vacuum. The product was recrystallized twice from n-

hexane. The red product was further purified using column chromatography (silica gel, EtOAc). (9.07 g, yield:78%). ¹H NMR (300 MHz, CDCl₃, δ), (TMS, ppm): 1.50-1.95 (8H, C-CH2-C), 3.69 (2H, CH2OH), 4.00 (2H, ArO-CH2-C), 6.58 (2H, ArH), 7.02 (2H, ArH), 7.29 (1H, ArH).

Synthesis of 6-(4-((2,6-difluorophenyl) diazenyl)-3,5-difluorophenoxy) hexyl methacrylate (FAZO)

FAzoC₆OH (7.4 g, 20 mmol) and triethylamine(4.04 g, 40 mmol) were mixed in anhydrous CH₂Cl₂ (100 mL) in an ice bath. A solution of 2.28 g (22 mmol) of methacryloyl chloride in anhydrous CH₂Cl₂ (20 mL) was added dropwise over 2 h under dry argon. The completion of the reaction was checked by thin layer chromatography using ethyl acetate as eluent. Then the reaction mixture was filtered and the solution was distilled under vacuum. The red product was further purified using column chromatography (silica gel, EtOAc). The FAZO was characterized by ¹H NMR. ¹H NMR (300 MHz, CDCl₃, δ), (TMS, ppm): 1.38-1.91 (8H, C–CH2–C), 1.91-2.00 (3H,CH₃-C=CH₂), 4.01 (2H, -CH₂OCO-) , 4.16 (2H, ArO-CH2-C) ,5.56 (1H, CH₃-C=CH₂) , 6.10(1H, CH₃-C=CH₂), 6.58 (2H, ArH, 6.96-7.12 (2H, ArH) , 7.26-7.39 (1H, ArH)

Synthesis of 6-(4-(phenyldiazenyl) phenoxy) hexyl methacrylate (AZO), and 6-(4-((4-cyanophenyl) diazenyl) phenoxy) hexyl methacrylate (AZOCN)

The synthesis method of AZO and AZOCN were the same as the FAZO, characterized by ¹H NMR.

¹H NMR (AZO, 300 MHz, CDCl₃) δ 7.92 (4H, ArH), 7.47 (3H, ArH), 7.00 (2H, ArH), 6.10 (CH₃-C=C<u>H</u>₂), 5.63 – 5.47 (1H, CH₃-C=C<u>H</u>₂), 4.17 (2H, ArO-CH2-C), 4.05 (2H, -C<u>H</u>₂OCO-), 2.01 – 1.91 (3H, C<u>H</u>₃-C=CH₂), 1.91 – 1.79 (2H, ArO-CH2-C<u>H</u>₂-), 1.79 – 1.67 (2H, -C<u>H</u>₂CH₂OCO-), 1.61 – 1.41 (4H, -CH₂-).

¹H NMR (AZOCN, 300 MHz, CDCl₃) δ 7.95 (4H, ArH), 7.86 – 7.72 (2H, ArH), 7.10 – 6.94 (2H, ArH), 6.10 (1H, CH₃-C=C<u>H₂</u>), 5.62 – 5.49 (1H, CH₃-C=C<u>H₂</u>), 4.17 (2H, ArO-CH2-C), 4.07 (2H, -C<u>H₂OCO-</u>), 2.03 – 1.91 (3H, C<u>H₃-C=CH₂</u>), 1.91 – 1.80 (2H, ArO-CH2-C<u>H₂</u>-), 1.80 – 1.68 (2H, -C<u>H₂CH₂OCO-</u>), 1.60 – 1.41 (4H, -CH₂-).

Sythesis of the macroinitiator PEG₁₁₃-Br

In a typical reaction, PEG₁₁₃ (25 g, 5 mmol) and triethylamine(1.21 g, 12 mmol) were

mixed in anhydrous CH_2Cl_2 (100 mL) in an ice bath. A solution of 2.37 g (11 mmol) of 2-bromopropionyl bromide in anhydrous CH_2Cl_2 (20 mL) was added dropwise over 2 h under dry argon. The solution was then allowed to warm to room temperature and was stirred for 48 h. The precipitate was removed by filtration. The filtrate was poured into water and the water phase was extracted with CH_2Cl_2 three times. The combined organic phase was further washed with 1.0 M HCl and 1.0 M NaOH aqueous solutions successively and dried over anhydrous Na₂SO₄. After solvent removal, the crude product was purified twice by dissolving in 10 mL of CH_2Cl_2 and precipitation with 300 mL of diethyl ether. The white solid was collected by filtration, and dried in a vacuum oven for 24 h. ¹H NMR (300 MHz, CDCl₃) δ 4.33 (2H, $-CH_2OC=O$), 3.64 (-OCH2-CH2O-,450H), 3.38 (3H, CH_3OCH2-), 1.94 (6H, $-C(CH_3)_2$ -Br). The MALDI-TOF mass spectra was listed in the Figure S1A.

Synthesis of PEG-b-PolyAZO.

The amphiphilic azobenzene-containing block copolymers PEG-b-PolyAZO were prepared through atom transfer radical polymerization (ATRP) initiated by a macroinitiator (PEGBr). PEGBr was obtained through the reaction of PEG monomethyl ether with 2-bromo-2-methylpropionyl bromide. The repeat unit number of PEGBr was estimated to be 113 from the ¹H NMR spectrum and the structure was confined by matrix-assisted laser desorption/ionization time-of-flight mass spectrometer MALDI-TOF mass spectra (Figure S1A). Azobenzene-containing monomers 6-(4-((2,6difluorophenyl) diazenyl)-3,5-difluorophenoxy) hexyl methacrylate (FAZO), 6-(4-(phenyldiazenyl) phenoxy) hexyl methacrylate (AZO), 6-(4-((4-cyanophenyl) diazenyl) phenoxy) hexyl methacrylate (AZOCN), was synthesized according to the method described in Supporting Information. The synthesis of PEG₁₁₃-b-PFAZO₇₈ is given below as a typical example. PEG-b-PFAZO_x copolymers were then prepared feed ratios of the monomer through ATRP with same to PEGBr ([monomer]₀:[PEGBr]₀:[CuBr]₀:[PMDETA]₀=150:1:2:4), but different polymerization time. PEGBr (55.0 mg, 0.01 mmol) and CuBr (2.86 mg, 0.02 mmol) were added to a 5 mL ampoule flask. The flask was degassed and back-filled with argon three times. Anisole (1.0 mL), FAZO (657.0mg, 1.50mmol) PMDETA (6.94mg, 0.04 mmol), were added to the flask through gastight syringes. After it was degassed by three freezepump-thaw cycles, the flask was immersed in an oil bath at 80 °C for polymerization under argon atmosphere. After 14 h, the reaction was stopped by diluting with THF, and the mixture was passed through an alumina column to remove the catalyst. The polymer was purified twice by precipitation in diethyl ether, collected by filtration, and dried in a vacuum oven for 24 h. PEG₁₁₃-b-PAZO_y, PEG₁₁₃-b-PAZOCN_z, were synthesized using the same method.

Estimating of the repeated units of AZO (n) in the PEG-b-PolyAZO

¹H NMR spectra of the PEG-b-PolyAZO block copolymers prepared *via* ATRP chain-extension were shown in Figure S1B. The average number of azobenzene monomer units (n_{FAZO} , n_{AZO} , n_{AZOCN}) was calculated respectively by Formula S1 based on the integral values of protons at PEG and protons at azobenzene in Figures S1B. The number average molecular weight of PEG-b-PolyAZO calculated by ¹H NMR ($M_{n,NMR}$) was obtained using Formula S2. The calculation formulas are as follows:

$$n_{FAZO} = [(I_1/2)/(I_b/4)] \times 113;$$

$$n_{AZO} = [(I_1/2)/(I_b/4)] \times 113;$$

$$n_{AZOCN} = [(I_q/2)/(I_b/4)] \times 113 \qquad \dots \text{(Formula S1)}$$

 $M_{n,NMR} = M_{PEG-Br} + n(azobenzene) \times M(azobenzene) \dots (Formula S2)$

Where, M_{PEG-Br} : the molecular mass of the macroinitiator; I_i : integral of the protons in PEG-b-PFAZO at 6.23-6.64 ppm; I_i : integral of the protons in PEG-b-PAZO at 6.76-7.03 ppm; I_q : integral of the protons in PEG-b-PAZOCN at 6.75-7.08 ppm; I_b : integral of the protons in PEG-b-PFAZO at 3.65 ppm.

Self-assembly of PEG-b-PolyAZO.

In a typical procedure, the block copolymer was first completely dissolved in 1,4dioxane, with an initial concentration of 1.0 mg/mL. The polymer solution was then filtered through a PTFE filter with 0.22 μ m pore size to remove any dusts to obtain the stock solution. Milli-Q water was then slowly added (0.1 mL/h) to 1.0 mL of the stock solution under gentle shaking at 25°C until the water content reached a predetermined value.

Characterization

The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were determined by a TOSOH HLC-8320 size exclusion chromatography equipped with refractive-index and UV detectors using two TSKgel Super Mutipore HZ-N (4.6×150 mm, 3 µm beads size) columns arranged in series, and it can separate polymers in the molecular weight range from 500~1.9×10⁵ g/mol. THF was used as the eluent at a flow rate of 0.35 mL/min at 40 °C. Data acquisition was performed using EcoSEC software, and molecular weights were calculated with polymethyl methacrylate (PMMA) standards. ¹H NMR spectra were collected using a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature, NMR samples were prepared with a concentration of ~20 mg/mL in CDCl₃. Transmission electron microscopy (TEM) was observed on HITACHI HT7700 at a 120 kV accelerating voltage. Samples for TEM observation were prepared by placing a drop of self-assembled polymer solution onto a carbon-coated copper grid. After 30 s, the excess fluid was removed with a piece of filter paper. Then a drop of staining agent phosphotungstic acid (1 wt%) was placed on the grid, and after 30 s, the excess solution was removed with a piece of filter paper and the grid was left to dry under the ambient conditions. Because of the particularity and novelty of the huge tubular shape, most of the reported tubular vesicles have been characterized only by electron microscopy so far. Scanning electron microscopy (SEM) images were taken with a HITACHI S-4700 cold field-emission scanning electron microscope operated at 15 KV. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurement was performed using a Bruker Autoflex III (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Ultraviolet visible (UV-vis) absorption spectra were determined on a Hitachi U-3900 spectrophotometer at room temperature. The light source used for the optical response test was a diode pumped solid state laser (DPSSL), purchased from LASEVER INC.

The model of the green laser is LSR532NL-500, with 532 nm wavelength, 500 mW maximum output power, and the beam diameter on the sample was 4 mm. The model of the blue laser is LSR405NL-250, with 405 nm wavelength, 250 mW maximum output power, and the beam diameter on the sample was 8mm.



Scheme S1. Synthesis routes and chemical structures of PEG-b-PolyAZO: (A) PEG₁₁₃b-PFAZO_x, (B) PEG₁₁₃-b-PAZO_y, (C) PEG₁₁₃-b-PAZOCN_z



Figure S1. (A) MALDI-TOF mass spectrum of the macroinitiator PEG₁₁₃-Br, (B) ¹H NMR spectra for (a) PEG₁₁₃-b-PFAZO_x, (b) PEG₁₁₃-b-PAZO_y, (c) PEG₁₁₃-b-PAZOCN_z

prepared via ATRP chain-extension using PEG₁₁₃-Br as the macro-ATRP initiator.



Figure S2. GPC curves of (a) PEG_{113} -b-PFAZO_x, (b) PEG_{113} -b-PAZO_y, (c) PEG_{113} -b-PAZOCN_z via ATRP chain-extension using PEG_{113} -Br as the macro-ATRP initiator.

sample	$M_{\rm n}$ a(g/mol)	$M_{\rm n}^{\rm b}({\rm g/mol})$	$M_{ m w}\!/M_{ m n}{}^{ m b}$	hydrophobic
				character ^c (wt %)
PEG ₁₁₃ -b-PFAZO ₂₀	13800	22700	1.08	63.5
PEG ₁₁₃ -b-PFAZO ₃₅	20400	26500	1.14	75.1
PEG ₁₁₃ -b-PFAZO ₅₁	27400	29700	1.19	81.5
PEG ₁₁₃ -b-PFAZO ₇₈	39200	37700	1.32	87.2
PEG ₁₁₃ -b-PFAZO ₁₀₀	48900	51600	1.40	89.8
PEG ₁₁₃ -b-PAZO ₂₂	13200	22400	1.20	61.3
PEG ₁₁₃ -b-PAZO ₄₆	22000	36800	1.12	76.8
PEG ₁₁₃ -b-PAZO ₆₄	28600	42300	1.18	82.2
PEG ₁₁₃ -b-PAZO ₁₁₁	45800	52500	1.21	88.9
PEG ₁₁₃ -b-PAZOCN ₂₁	13300	32100	1.12	61.7
PEG ₁₁₃ -b-PAZOCN ₃₇	19600	45500	1.17	74.0
PEG ₁₁₃ -b-PAZOCN ₅₉	28200	48400	1.19	81.9
PEG ₁₁₃ -b-PAZOCN ₆₈	31700	49700	1.19	83.9

Table S1. Characterization data of diblock copolymers PEG_{113} -b-PFAZO_x, PEG_{113} -b-PAZO_y and PEG_{113} -b-PAZOCN_z with different molecular weight

a: Measured by ¹H NMR spectra. b: Determined by GPC traces. c: hydrophobic weight fraction determined by ¹H NMR spectra.



Figure S3. TEM images (stained with phosphotungstic acid) of self-assembled morphologies of (a) PEG_{113} -b-PFAZO₂₀, (b) PEG_{113} -b-PFAZO₃₅, (c) PEG_{113} -b-PFAZO₅₁, (d) PEG_{113} -b-PFAZO₇₈, (e) PEG_{113} -b-PFAZO₁₀₀, and (f) PEG_{113} -b-PFAZO₁₀₀ at a 200 nm scale in water/1,4-dioxane (37.5% water content). The initial concentration was 1.0 mg/mL in all cases.

In Figure S3, for the PEG₁₁₃-b-PFAZO₂₀ and PEG₁₁₃-b-PFAZO₃₅, only sphere micelles with diameters of ~25 nm were obtained (Figure S3 a, b). For the PEG₁₁₃-b-PFAZO₅₁, vesicular structures with diameters from 90 nm to 150 nm, a wall thickness of ~30 nm were formed (Figure S3 c). As the hydrophobic block ratio reached 87.2% (PEG₁₁₃-b-PFAZO₇₈), it was interesting to observe tadpole-shaped tubular polymersomes with one big vesicle of ~470 nm at one end joined by tubular tail with a diameter of ~200 nm and a wall thickness of ~37 nm (Figure S3 d). Further increasing the hydrophobic block ratio to 89.8% (PEG₁₁₃-b-PFAZO₁₀₀), double-layer type tubular polymersomes were broadly appearing with a diameter of ~210 nm and a wall thickness of ~47 nm (Figure S3 e, f).



Figure S4. (A) DSC 2nd heating traces (a) PEG₁₁₃-b-PFAZO₇₈, (b) PEG₁₁₃-b-PAZO₆₄, (c) PEG₁₁₃-b-PAZOCN₅₉ in the bulk. Procedure segments: ramp 10 °C/min to 180 °C; isothermal 1.0 min; ramp 10 °C/min to -80 °C; isothermal 2.0 min; ramp 10 °C/min to 180°C. (B) POM of the freeze-dried tubular polymersomes samples (a) PEG₁₁₃-b-PAZO₇₈, (b)PEG₁₁₃-b-PAZO₆₄, (c) PEG₁₁₃-b-PAZOCN₅₉ at room temperature.

From DSC, PEG₁₁₃-b-PFAZO₇₈ showed no obvious thermal transitions but a glass transition at 27.4°C, indicating the lack of liquid crystal (LC) structure. PEG₁₁₃-b-PAZO₆₄ and PEG₁₁₃-b-PAZOCN₅₉ showed two thermal transitions corresponding to the melting of PEG (35.0 °C, 35.7 °C) and liquid crystal to isotropic phase transition of PolyAZO (53.73 °C for PEG₁₁₃-b-PAZO₆₄, 159.2 °C for PEG₁₁₃-b-PAZOCN₅₉). PEG₁₁₃-b-PAZOCN₅₉ appeared sharper melting peaks and higher enthalpies indicating the existence of highly ordered LC stuctures.

From POM, image of the PEG_{113} -b-PAZO₆₄, PEG_{113} -b-PAZOCN₅₉ exhibited bright patterns, indicating the presence of the liquid crystal (LC) structure in the membrane of tubular polymersomes. Meanwhile the relative dark patterns of PEG_{113} -b-PFAZO₇₈ revealed the absence of LC structure.



Figure S5. TEM images of aggregates formed by PEG_{113} -b-PFAZO₇₈ in water /1,4dioxane with different water content (a) 16.6%, (b) 27.1% (c) 34.4%, (d) tadpoleshaped tubular polymersomes with multi-tails, when the water content was 27.1%. The initial concentration was 1.0 mg/mL and the speed of adding water was 0.10 mL/h in all cases. The inset image in Figure S5a means the TEM images of PEG_{113} .b-PFAZO₇₈ in water /1,4-dioxane with 16.6% water content at a large scale. The section in red circle was magnified to get a clear image. TEM images of the initial spherical vesicles (e) and the heads of the tadpole-shaped tubular polymersomes (f, g) with water content from 16.6 % (e), 27.1% (f) to 37.5% (g). The inset in (e) (f) (g) means distribution profiles of spherical vesicles diameter, and head diameter of tubular polymersomes obtained by statistical and calculating methods corresponding to TEM images.

The statistical and calculating methods were as follows: the corresponding size of every aggregate (Di) in TEM image was measured, such as the diameter, the wall thickness, etc. The average sizes (D_n) were calculated by the following formula:

$$D_{n} = \sum_{i=1}^{n} Di / n$$

where n represents total number of the measuring object, Di represents size of every object.

Water content (%)	Average diameter of head (nm)	Average diameter of tail (nm)	Average wall thickness (nm)
16.6 %	1000		
27.1%	710	250	72
34.4 %	550	220	48
37.5%	470	200	37
60.0%	470	200	33

Table S2. Calculated average diameters of head and tail parts of tubular polymersomes and wall thickness corresponding to the self-assemblies in Figure 2.

As the water content increasing to 27.1%, the spherical polymersome with a diameter of about 1000 nm began to transfer into tadpole-shaped polymersome consisting of a vesical head with the diameter of about 710nm and a short tubular tail with the diameter of about 250nm (Figure S5b). As water content continued to increase, the head part of the tadpole-shaped polymersome became smaller and the tail part became slimmer and longer. For example, the diameter of head and tail part decreased to around 550nm, 220nm respectively, as the water content reaching 34.4% (Figure S5c). When the water content was 37.5%, the diameters of head and tail part continued to decrease to 470nm, 200 nm respectively, but the change was not too obvious when continued to add water. This is because dioxane came out from the hydrophobic layer of the membrane progressively during adding water, so that the chain mobility of core-forming block became slow, restricting morphological change. There can also find that the average wall thickness was getting thinner gradually during adding water, which means the stretching of the azo-polymer chains in the tubular polymersomes decreased gradually.



Figure S6. TEM images of aggregates formed by PEG_{113} -b-PFAZO₇₈ in water/1,4dioxane with different water content (v/v): (a) 37.5%, (b) 50%, (c, d) 60%, (e) c, d after dialysis against ultrapure water. (f) SEM images of e. The initial concentration was 1.0 mg/mL and the speed of adding water was 0.1 mL/h in all cases. The insets represent the corresponding images at large scales.



Figure S7. UV–vis spectra of the 0.05mg/mL PEG₁₁₃-b-PFAZO₇₈ tubular polymersomes aqueous solution under the irradiation of (a) green light (532 nm), the initial state is corresponding to the equilibrium state under 405nm light irradiation (b)

blue light (405 nm). The out power of the green laser light was 335 mW, the blue laser light was 86 mW. Unless other illustration, the next experiments were operated under the same intensity irradiation.



Figure S8. The reversible absorbance changes of $0.05 \text{mg/mL PEG}_{113}$ -PFAZO₇₈ aggregates aqueous solution at 351 nm under the alternative green light irradiation for 1 min and blue light irradiation for 10s.



Figure S9. Changes in the light transmittance of the tubular polymersome solution of PEG_{113} -b-PFAZO₇₈ under alternant irradiation with blue and green light. The initial

concentration in 1,4-dioxane was 1.0 mg/mL and the mixture solvent was composed of 1.0 mL1,4-dioxane and 0.6 mL water.



Figure S10. TEM images of the tubular polymersomes of the PEG_{113} -b-PFAZO₇₈ formed in the water/dioxane (0.6/1, v/v) solvent. (a) initial aggregates; (b) aggregates formed after 532nm green light irradiation for 5 min (trans-cis isomerization); (c) aggregates formed after 405 nm blue light irradiation for 5 min (cis-trans isomerization).

The initial concentration in 1,4-dioxane



Figure S11. TEM images of the tubular polymersomes of the PEG_{113} -b-PAZOCN₅₉ formed in the water/ dioxane (0.6/1, v/v) mixed solvent, initial concentrations: 1.0 mg/ mL in dioxane solvent. (a, d) initial aggregates; (b, e) aggregates formed after 405 nm

blue light irradiation for 5 min (trans-cis isomerization); (c, f) aggregates formed after 532 nm green light irradiation for 5 min and standing for 2 h at dark (cis-trans isomerization). The inset picture in a, b, c are the enlarged view of the tubular polymersomes polysomes at the end at initial state, after irradiation with 405 nm blue light and 532 nm green light.

The diameters of the PEG₁₁₃-b-PAZOCN₅₉ tubular polymersomes were 170 nm, 380 nm and 310 nm at initial state, cis-state and trans-state, respectively, which suggested a significant back-and-forth change. Meanwhile, the sharp hemi ellipsoidal shapes of the terminal in the tubular polymersomes changed into smooth hemispherical shapes, and returned to ellipsoidal shapes by alternant irradiation with green/blue light. The possible reason for shape change was given here. Because the dipole moment of trans-AZOCN (8.467 D) is greater than that of cis one (5.570D) (Figure S12), we inferred that the morphologic change of the tubular polymersomes of PEG₁₁₃-b-PAZOCN₅₉ during irradiation might mainly attributed to re-arrangement of 4-cyanoazobenzenes unit in the be polymersomes. The orientation of planar trans-isomer of 4-cyanoazobenzenes usually preferred being parallel to the membrane for forming LC phase in selfassembled aggregates (Figure S4). The light-triggered structure change from planar trans-azobenzene to cis one might induce the LC-isotropic phase transition in the polymersome membrane, further resulting in morphological change from sharp hemi ellipsoidal shapes to smooth hemi spherical ones.



Figure S12. Electron cloud distribution and dipole moment of o-fluoroazobenzene derivative (FAZO) and p-cyanoazobenzene derivative (AZOCN) calculated using the three parameter hybrid B3LYP density functional method with the extended basis set 6-311++G(d,p) implemented in the GAUSSIAN 09 package.



Figure S13. UV–vis spectra of the 0.05mg/mL aqueous solution of PEG_{113} -b-PFAZO₇₈ tubular polymersomes before and after reducing with hydrazine hydrate (5% volume ratio in aqueous solution). The inset represents the solution changes in color from yellow to colorless after reducing with hydrazine hydrate.