Supplementary Information for

### Reversible Photoisomerization of Azobenzene-Containing Polymeric System Driven by Visible Light

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#### 1. Materials

4-Hydroxy-4'-dimethylaminoazobenzene (>98%, TCI), 6-chloro-1-hexyne (98%, Alfa Aesar), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%, Aldrich), methacryloyl chloride (95%, Shanghai Aladdin Reagent Co. Ltd.), α-bromoisobutyryl bromide (98%, Aldrich), potassium carbonate ( $K_2CO_3$ ) ( $\geq$ 99%, Shanghai Sinopharm Chemical Reagent Co. Ltd.), were used as received without further purification. Poly(ethylene glycol) methyl ether (PEG) with an average molecular weight of ca. 2000 Da (Aldrich) was dried for 48 h at 60 °C in a vacuum oven before use. Copper(I) bromide (CuBr) (98%, Aldrich) was firstly purified by stirring with acetic acid for several hours, filtrating, and then washing with acetic acid, ethanol and diethyl ether in succession until it turned into white, finally stored under vacuum before use. Anisole, dimethyl formamide (DMF), triethylamine (TEA) and dichloromethane (DCM) from Shanghai Sinopharm Chemical Reagent Co. Ltd., were treated with calcium hydride and distilled before use. Acetic acid, diethyl ether, methanol, ethanol etc. were from Shanghai Sinopharm Chemical Reagent Co., Ltd, and distilled water was used as received.

#### 2. Instruments and Measurements

#### Nuclear Magnetic Resonance (NMR)

<sup>1</sup>H NMR spectra were recorded on a Varian Mercury plus 400 NMR spectrometer (400 MHz) with deuterated chloroform (CDCl<sub>3</sub>) as solvents at 293 K. The chemical shifts were referenced to residual peaks of deuterated solvents: CDCl<sub>3</sub> (7.26 ppm).

#### **Gel Permeation Chromatography (GPC)**

The molecular weight and polydispersity index (PDI) of the samples were determined by gel permeation chromatography/multi-angle laser light scattering (GPC-MALLS). The gel permeation chromatography system consisted of a Waters degasser, a Waters 515 HPLC pump, a 717 automatic sample injector, a Wyatt Optilab DSP differential refractometer detector, and a Wyatt miniDAWN multi-angle laser light scattering detector. Three chromatographic columns (styragel HR3, HR4, and HR5) were used in series. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min at 30 °C. The refractive index increment dn/dc was determined with Wyatt Optilab DSP differential refractometer at 690 nm.

#### **Dynamic Light Scattering (DLS)**

DLS measurements were performed on a Malvern Zetasizer NanoS apparatus equipped with a 4.0 mW laser operating at  $\lambda = 633$  nm. All samples were measured at a scattering angle of 90° with polymer concentration of about 0.5 mg/mL at 25 °C. Before testing, the dust was firstly eliminated by filtering the sample solutions through some absorbent cotton. The sample solutions were placed in the cell for at least 15 min prior to the measurement to allow for thermal equilibration and chemical equilibration.

#### **Transmission Electron Microscopy (TEM)**

TEM measurements were performed with a JEOL JEM-100CX-II instrument at a voltage

of 200 kV. The specimen was prepared by directly drop-casting the sample solution onto a carbon-coated copper grid and then air-drying at room temperature for 48 h before measurement.

#### **UV-Vis Absorption Spectra**

The UV-Vis absorption of the sample solutions was measured at room temperature by using a Thermo Electron-EV300 UV-Vis spectrophotometer. The slit-width was set as 1 nm, and scan speed was set as 480 nm/min.

#### **Steady-State Fluorescence Emission Spectra**

The fluorescence emission spectra were recorded on a PTI-QM/TM/IM steady-state & time-resolved fluorescence spectrofluorometer (USA/CAN Photon technology international Int.). The optimal excitation wavelength of the sample solutions was set at 330 nm or 380 nm, which was chosen according to the maximum intensity obtained in the excitation spectra. The slit-width was set as 2 nm, and scan speed was set as 480 nm/min. The sample solutions were maintained in the fluorescent cell for 10 min prior to the measurement to allow for thermal equilibration.

#### Trans-to-Cis Photoisomerization induced by visible light at 450 nm

Visible light at 450 nm with a power density of 5 mW/cm<sup>2</sup> was obtained from LED irradiators (UVATA, UV LED Spot Light Source-UP II).

#### 3. Synthesis and Characterization of PEG-b-PDMA-Azo



Scheme S1 Synthesis route of PEG-Br (A), HMA-DMA-Azo (B) and PEG-*b*-PDMA-Azo (C).

(A) **PEG-Br:** To a dichloromethane solution of PEG-2k (4.0 g, 2 mmol) and triethylamine (202 mg, 2 mmol, 1.0 equiv.) at ca. 0 °C, the dichloromethane solution containing  $\alpha$ -bromoisobutyryl bromide (919 mg, 4.0 mmol, 2.0 equiv.) was slowly added dropwise for about 1 h. After the addition was completed, the reaction mixture was left to react for another 24 h at room temperature under stirring. The resulting solution was washed with deionized water for three times to remove the water-soluble triethylamine hydrochloride. After being dried with Na<sub>2</sub>SO<sub>4</sub>, the organic phase was concentrated to 15

mL, and then precipitated into 200 mL of ice diethyl ether for twice. Finally, the product was collected and dried in vacuum oven at 40 °C for 24 h, yielding 3.60 g (1.68 mmol, 83.7%) as a white solid.  $M_n$  (NMR) = 2.15 kDa,  $M_n$  (GPC) = 2.23 kDa,  $M_w/M_n$  = 1.03.

<sup>1</sup>**H** NMR (CDCl<sub>3</sub>, 400 MHz) (*Fig. S1A*):  $\delta_{\rm H}$  (ppm) = 4.31 (m, -CH<sub>2</sub>OOC-, 2H), 3.63 (m, -OCH<sub>2</sub>CH<sub>2</sub>O-, 176H), 3.36 (s, CH<sub>3</sub>O-, 3H), 1.92 (s, -OOCC(CH<sub>3</sub>)<sub>2</sub>-, 6H).

(B) HMA-DMA-Azo: According to our previous literature,<sup>1</sup> the brief synthesis 6-(4-(4-dimethylaminophenylazo) of phenoxy)-hexyl procedure methacrvlate (HMA-DMA-Azo) was as follows. The dichloromethane solution of methacryloyl chloride (1.57 g, 15 mmol, 2.0 equiv.) was slowly added dropwise to a dichloromethane solution containing 4-dimethylamino-4'-(6-hydroxy hexyloxy) azobenzene (2.56 g, 7.5 mmol) and triethylamine (0.76 g, 7.5 mmol, 1.0 equiv.) at ca. 0 °C for about 1 h. The reaction mixture was left to react for another 24 h at room temperature under stirring. The resulting solution was washed in series with 1 M HCl aqueous solution, deionized water, 1 M NaOH aqueous solution, and deionized water for three times. After being dried with Na<sub>2</sub>SO<sub>4</sub>, the organic phase was concentrated to 10 mL, and then precipitated into 200 mL of methanol/water (1/3, v/v) for twice. Finally, the product was collected and dried in vacuum oven at 40 °C for 24 h to yield 2.6 g (6.35 mmol, 83%) as a yellow-brown solid.

<sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz) (*Fig. S1B*):  $\delta_{\rm H}$  (ppm) = 7.84 (m, 4H), 6.96 (m, 2H), 6.76 (d, J = 8.74 Hz, 2H), 6.10 (m, 1H), 5.55 (m, 1H), 4.16 (t, J = 6.59, 13.19 Hz, 2H), 4.02 (t, J = 6.44, 12.88 Hz, 2H), 1.94 (m, 3H), 1.30-1.90 (m, 8H).

(C) **PEG-b-PDMA-Azo**: The amphiphilic diblock copolymer of PEG-*b*-PDMA-Azo has been synthesized by atom-transfer radical polymerization (ATRP), and the detailed synthesis procedure was as follows. PEG-Br (107 mg, 0.05 mmol) and HMA-DMA-Azo

(Monomer 1) (2.05 g, 5 mmol) were dissolved in 15.0 mL of anisole, and then degassed and filled with argon. Cu(I)Br (22 mg, 0.15 mmol) and HMTETA (82  $\mu$ L, 0.3 mmol) were successively added. The mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum, and placed in an oil bath preheated at 80 °C for 24 h. Then the resulting solution was passed through a neutral alumina column to remove the copper catalyst. The filtrate was concentrated to 10 mL, and then precipitated into 200 mL of methanol for three times. The product was collected and dried in vacuum oven at 40 °C for 24 h. Yield: 900 mg (45%). M<sub>n</sub> (NMR) = 16.5 kDa, M<sub>n</sub> (GPC) = 21.4 kDa, M<sub>w</sub>/M<sub>n</sub> = 1.07.

<sup>1</sup>**H** NMR (CDCl<sub>3</sub>, 400 MHz) (*Fig. S1C*):  $\delta_{\rm H}$  (ppm) = 7.79, 6.88, 6.69 (s, protons on Azo group), 3.90 (s), 3.64 (s, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.38 (s, CH<sub>3</sub>O-), 2.98 (s, (CH<sub>3</sub>)<sub>2</sub>N-), 2.04 (s), 1.30-1.90 (m), 0.80-1.10 (m).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz) (*Fig. S2*):  $\delta_{\rm C}$  (ppm) = 26.1, 28.3, 29.4, 40.5 (N(*C*H<sub>3</sub>)<sub>2</sub>), 65.2 (*C*H<sub>2</sub>), 68.2 (*C*H<sub>2</sub>(hexyl)-O), 70.8 (O-*C*H<sub>2</sub>-*C*H<sub>2</sub>-O), 111.8 (*C*H(Ar) close to N(*C*H<sub>3</sub>)<sub>2</sub>), 114.8 (*C*H(Ar) close to O-hexyl), 124.7 (*C*H(Ar) close to N=N), 143.9 & 147.4 (*C*(Ar)-N=N), 152.1 (*C*(Ar)-N(*C*H<sub>3</sub>)<sub>2</sub>), 160.6 (*C*(Ar)-O), 177.7 (*C*=O).

**FTIR** (KBr) (*Fig. S3*): v (cm<sup>-1</sup>) = 549, 821/839, 944, 1152/1244 (*C-O*), 1364 (*C-N*), 1444/1471, 1500/1518 (*N=N*), 1600 (*C=C*), 1724 (*C=O*), 2860/2934 (*C-H*), 3441.



**Fig. S1** <sup>1</sup>H NMR spectra of PEG-Br (A), HMA-DMA-Azo (B) and PEG-*b*-PDMA-Azo (C) in CDCl<sub>3</sub>.



Fig. S2 <sup>13</sup>C NMR spectrum of PEG-*b*-PDMA-Azo in CDCl<sub>3</sub>.



Fig. S3 FTIR spectrum of PEG-*b*-PDMA-Azo.

#### 4. Self-Assembly of Vesicles

1 mL THF solution containing 5 mg PEG-*b*-PDMA-Azo was slowly dropped into 5 mL of deionized water under vigorous stirring, followed by dialysis in a 3500 Da dialysis bag against deionized water to remove THF. After 48 h, the volume of the solution was increased to 10 mL to obtain an aggregate solution with a concentration of about 0.5 mg/mL for further experiments.

#### 5. Supplemented Figures

### PEG-*b*-PDMA-Azo $M_n = 21.4 \text{ kDa}$ $M_w/M_n = 1.07$ **PEG-Br** $M_n = 2.23 \text{ kDa}$ $M_w/M_n = 1.03$ **PEG-Br** $M_w/M_n = 1.03$

#### 5.1. GPC curves of PEG-b-PDMA-Azo copolymer

**Fig. S4** The GPC curves of PEG-Br macroinitiator and PEG-*b*-PDMA-Azo diblock copolymer.

#### 5.2. No isomerization for PEG-b-PDMA-Azo and its vesicles upon UV



**Fig. S5** (A) UV-Vis spectra of the THF solution of PEG-*b*-PDMA-Azo (c = 0.05 mg/mL) before and after UV irradiation for 30 min and (B) UV-Vis spectra of the vesicular aqueous solution (c = 0.05 mg/mL) at the initial state, after UV irradiation for 30 min or after stirring in the dark for 30 min.

As shown in **Fig. S5A**, no pronounced absorbance variation is observed for the THF solution of this copolymer irradiated by UV light for 30 min. Whereas the vesicular aqueous solution is irradiated by UV light for 30 min or stirred in the dark for 30 min, we note that there is an enhanced absorbance accompanied by a large bathochromic shift (~30 nm) of the absorption band (**Fig. S5B**), which can be attributed to the thermally induced rearrangement of DMA-Azo groups in the vesicles under UV irradiation or stirring in the dark. Furthermore, no significant absorbance variation after UV irradiation and stirring in the dark is observed for the vesicles. The results indicate that UV light cannot induce the photoisomerization transitions of this copolymer and its vesicular assemblies.

# 5.3. Critical aggregation concentration (CAC) of PEG-*b*-PDMA-Azo determined by fluorescence method



**Fig. S6** (A) Steady-state fluorescence spectra of vesicular aqueous solution with different concentrations (from 0.001 mg/mL to 0.50 mg/mL) and (B) its fluorescence intensity at 536 nm as a function of concentration of vesicular aqueous solution

Owing to its AIE effect, the critical aggregation concentration (CAC) of this copolymer was determined to be approximately 0.04 mg/mL by measuring the fluorescence at 536 nm of azobenzene chromophores in the copolymer aqueous solution with increasing concentrations (*Fig. S6*).

## 5.4. PEG-*b*-PDMA-Azo in THF upon Vis-450 irradiation and stirring in the dark



**Fig. S7** UV-Vis spectra of the THF solution of PEG-*b*-PDMA-Azo (c = 0.05 mg/mL) at the initial state, after Vis-450 irradiation for 10 min, and after stirring in the dark for 1 h.

5.5. Visible light-induced *trans-cis* photoisomerization behavior of PEG-*b*-PDMA-Azo



**Fig. S8** UV-Vis spectra of the THF solution of PEG-*b*-PDMA-Azo (c = 0.05 mg/mL) after Vis-450 irradiation for 10 min and stirring in the dark for 1 h.

After visible light irradiation (ca. 450 nm), a remarkable absorbance decrease at about 410 nm ( $\pi$ - $\pi$ \* transition of the *trans* DMA-Azo) and a slight absorbance increase at about 520 nm (n- $\pi$ \* transition of the *cis* DMA-Azo) are observed (*Fig. S8*). Moreover, after being stirred in the dark, the  $\pi$ - $\pi$ \* absorption increases remarkably with a slight decrease in the n- $\pi$ \* absorption, indicating that the photoisomerization of DMA-Azo groups undergoes a reversible change from the *cis*-form to the *trans*-form.

#### 5.6. Fluorescence change of the vesicles upon Vis-450 irradiation and



stirring in the dark

**Fig. S9** The fluorescence spectra of the vesicular aqueous solution at the initial state, after Vis-450 irradiation for 10 min and stirring in the dark for 1 h. The concentration of vesicular aqueous solution was 0.20 mg/mL.

#### 5.7. Reversible size change of the vesicles detected by DLS upon



alternative Vis-450 irradiation and stirring in the dark

**Fig. S10** (A) DLS profiles for the vesicles of PEG-*b*-PDMA-Azo before and after Vis-450 irradiation and (B) reversible size change of the vesicles detected by DLS upon alternative Vis-450 irradiation for 10 min and stirring in the dark for 1 h. Black bars represent the mean values (n = 4).

As shown in **Fig. S10A**, the hydrodynamic diameter of the vesicles decreases after being irradiated with visible light, which can be attributed to the conformational rearrangement of the *cis*-form DMA-Azo groups in the vesicles. Also, the reversible increase in hydrodynamic diameter of the vesicles can be achieved by being stirred in the dark due to the recovery of original conformational arrangement of *trans*-form DMA-Azo groups (**Fig. S10B**).



#### **5.8.** Photo-induced deformation behavior of the aggregates

**Fig. S11.** TEM images of the aggregates (A) before and (B) after being irradiated by visible light (450 nm) for 10 min.

As shown in *Fig. S11*, the photo-induced deformation behavior of the aggregates after being irradiated by visible light (450 nm) can be clearly observed. By irradiation with visible light (450 nm) for a period of time, the spherical aggregates can be elongated in the polarization direction and the deformation degree increases as the irradiation time increases.

#### 6. Reference

 R. J. Dong, B. S. Zhu, Y. F. Zhou, D. Y. Yan and X. Y. Zhu, *Angew. Chem. Int. Ed.*, 2012, **51**, 11633.