## **Cyclic Azobenzene-Containing Amphiphilic Diblock Copolymers: Solution Self-Assembly and Unusual Photo-Responsive Behaviors**

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### **Experimental Section**

### Materials

2,2'-Dihydroxybiphenyl (98.5%, J&K), 1,6-dibromohexane (analytical reagent, Shanghai Chemical Reagent Co. Ltd, Shanghai, China), sodium azide (99.5%, Aldrich), 3-ethynylaniline (>98%, Aldrich), 11-bromo-1-undecanol (98%, J&K), methacryloyl chloride (analytical grade, Shanghai Chemical Reagent Co. Ltd, Shanghai, China) were used as received. Copper (I) bromide (CuBr, chemical pure, Shanghai Chemical Reagent Co. Ltd, Shanghai, China) was purified via washing with acetic acid and acetone and then dried in vacuum at room temperature. *N*, *N*, *N'*, *N''*, *N''*-pentamethyldiethylenetriamine (PMDETA, 98%; Jiangsu Liyang Jiangdian Chemical Factory, China) was distilled three times under reduced pressure. Azobisisobutyronitrile (AIBN, chemical pure, Shanghai Chemical Reagent Co. Ltd, Shanghai, China) was recrystallized three times from ethanol and dried in vacuum at room temperature overnight. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) was synthesized according to the references <sup>[S1]</sup>. 2-(Dimethylamino) ethyl methacrylate (DMAEMA, 99.5%, Energy Chemical) was distilled under vacuum. All other reagents were used without further purification.



Scheme 1. Synthetic route towards homopolymer PDMAEMA<sub>m</sub>.

### Synthesis of poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA)

The macro-RAFT agent, PDMAEMA was prepared as follows: DMAEMA (1 mL, 6.00 mmol), AIBN (3.3 mg, 0.02 mmol), and CPDN (16.1 mg, 0.06 mmol) were dissolved in 0.25 mL anhydrous THF. The contents were purged with argon for 10 min to eliminate the oxygen. Then the ampule was flame-sealed and stirred in an oil bath by a thermostat at 70 °C for 2 h. Whereafter, the ampule was cooled at room temperature and opened afterwards. The polymer was obtained by precipitation in excess of hexane for three times and dried in a vacuum oven at 30 °C. The conversion of polymerization was determined gravimetrically.

Synthesis of poly[2-(dimethylamino)ethyl methacrylate]<sub>m</sub>-b-Poly(cyclic-AzoMMA)<sub>n</sub> (PDMAEMA<sub>m</sub>-b-PcyclicAzo<sub>n</sub>) The PDMAEMA<sub>m</sub>-*b*-PcyclicAzo<sub>n</sub> was prepared in anisole using the similar procedures of RAFT polymerization of DMAEMA, except the PDMAEMA was used as the macro-RAFT agent ([cyclicAzo]<sub>0</sub>:[AIBN]<sub>0</sub>:[macro-RAFT]<sub>0</sub> = 50:1:1). The copolymer was obtained by precipitation in excess of ether. The ratio of DMAEMA block length (m) to cyclicAzo block lengths (n) of copolymers were determined by adjusting the feeding molar ratio of monomer (cyclicAzo) to macro-RAFT agent (PDMAEMA) and reaction time. Two copolymers were obtained as follows: PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub>, PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>83</sub>. The resulting copolymers were confirmed by GPC, <sup>1</sup>H NMR, <sup>13</sup>C NMR and FTIR spectra.

### The estimation of the number of repeated units of DMAEMA (m) and cyclicAzo (n) in the PDMAEMA<sub>m</sub>-*b*-PcyclicAzo<sub>n</sub>

The number-average molecular weight ( $M_{n,NMR}$ ) and the number of repeated units of DMAEMA (m) of PDMAEMA were calculated by the <sup>1</sup>H NMR spectrum of the PDMAEMA in Figure S1(B) and the following equation S1 and equation S2:

$$M_{n,NMR} = (I_{2.5-2.7}/2)/(I_{7.4-8.2}/7) \times M_{DMAEMA} + M_{CPDN}$$
Equation S1  
m = (I\_{2.5-2.7}/2)/(I\_{7.4-8.2}/7)Equation S2

 $I_{2.5-2.7}$ : the integrations at 2.5-2.7 ppm in <sup>1</sup>H NMR relative to the -CH-N- (2H) of DMAEMA units in PDMAEMA.

 $I_{7.4-8.2}$ : the integrations at 7.4-8.2 ppm in <sup>1</sup>H NMR relative to the naphthyl moieties of RAFT agent (CPDN) at end groups in PDMAEMA.

 $M_{\text{DMAEMA}}$ : the molecular weight of DMAEMA monomer.

 $M_{\text{CPDN}}$ : the molecular weight of RAFT agent (CPDN).

From the <sup>1</sup>H NMR spectra of the PDMAEMA<sub>m</sub>-*b*-PcyclicAzo<sub>n</sub> in Figure S1(B), the number of the repeated units (n) of the cyclicAzo blocks could be calculated by following equation S3.

$$n = (I_{8.3-8.5})/(I_{2.5-2.7}/2) \times m$$
 Equation S3

 $I_{8,3-8,5}$ : the integrations at 8.3-8.5 ppm in <sup>1</sup>H NMR relative to the proton of 1,2,3-trazole.

# The self-assembly of PDMAEMA<sub>m</sub>-b-PcyclicAzo<sub>n</sub> in mixed solution of DMF and HAc/NaAc buffer solution

A typical self-assembly of the copolymer PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> was conducted as follow: PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> was first dissolved in DMF with an initiation concentration of 1 mg/mL, and then the resulting DMF solution of copolymer was filtered through a filter of 0.22  $\mu$ m pore size to remove dust. In general, a NaAc/HAc buffer solution (0.1M, PH=3) was added at a rate of 10  $\mu$ L/hour to a vial containing 2 mL of a stock solution of polymer in DMF as a common solvent, with an initial concentration of 1 mg/mL until the final water content reached 80 wt%. The stable sphere micelles were then obtained by dialyzing the micelle solution against NaAc/HAc buffer for 3 days to remove the organic solvent. The self-assembly of PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>83</sub> was also conducted according to the similar procedures.

### Characterizations

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as

the internal standard at room temperature. <sup>13</sup>C NMR spectrum was obtained on a Varian Mercury Plus spectrometer (100MHz) using CDCl<sub>3</sub> as the solvent. The number-average molecular weight  $(M_n)$  and molecular weight distribution  $(M_w/M_n)$  of the polymers were determined by a TOSOH HLC-8320 gel permeation chromatograph (GPC) equipped with a refractive-index detector (TOSOH), using TSKgel guardcolumn SuperH-H and TSKgel SuperHM-M×2 with measurable molecular weight ranging from  $7 \times 10^2$  to  $2 \times 10^5$  g/mol. These samples were calibrated with PS standards purchased from TOSOH. DMF + 0.01 mol/L LiBr was used as an eluent at a flow rate of 0.6 mL·min<sup>-1</sup> operated at 40 °C. Fourier transform infrared (FT-IR) spectrum was recorded on a Nicolette-6700 FTIR spectrometer. Ultraviolet visible (UV-vis) absorption spectra of the samples were determined on a Shimadzu UV-2600 spectrophotometer at room temperature. Snakeskin<sup>TM</sup> dialysis tubing was purchased from thermoscientific with a molecular weight cut off (MWCO) of 10,000 g/mol. Hydrodynamic radius (R<sub>h</sub>) was determined by DLS using a Wyatt Dynapro NanoStar. TEM was performed on a FEI Sphera microscope operating at 200 keV. TEM grids were prepared by depositing small (3.5  $\mu$ l) aliquots of sample onto grids (~ 2 min, Formvar stabilized with carbon (5-10 nm) on 400 copper mesh, Ted Pella Inc.) that had previously been glow discharged using an Emitech K350 glow discharge unit and plasma-cleaned for 90 s in an E.A. Fischione 1020 unit. The sample grid was then stained with 1% uranyl acetate solution, rinsed with water (~5 µL), and excess liquid was removed. Micrographs were recorded on a 2K X 2K Gatan CCD camera.

The first-order rate constant  $k_e$  of *trans*-to-*cis* photoisomerization was determined

by the Formula S1:

$$Ln[(A_{\infty}-A_{t})/(A_{\infty}-A_{0})] = -k_{e}t \quad (Formula S1)$$

Here  $A_{\infty}$ ,  $A_t$ , and  $A_0$  are absorbance at about 345 nm corresponded to the  $\pi$ - $\pi$ \* transition of *trans* isomers of azobenzene at infinite time, time t and time 0 with irradiation of 365 nm UV light (35  $\mu$ W/cm<sup>2</sup>) at room temperature, respectively.

The first-order rate constant  $k_{\rm H}$  of *cis-to-trans* recovery was determined by the Formula S2:

$$Ln[(A_{\infty}-A_{t})/(A_{\infty}-A_{0})] = -k_{H}t \quad (Formula S2)$$

Here  $A_{\infty}$ ,  $A_t$ , and  $A_0$  are absorbance at about 345 nm corresponded to the  $\pi$ - $\pi$ \* transition of *trans* isomers of azobenzene at infinite time, time t and time 0 in the dark at room temperature, respectively.



**Figure S1.** The GPC traces of the PDMAEMA<sub>101</sub>( $M_n = 13200 \text{ g/mol}, M_w/M_n = 1.16$ ), PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub>( $M_n = 22000 \text{ g/mol}, M_w/M_n = 1.32$ ) and PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>83</sub> ( $M_n = 33500 \text{ g/mol}, M_w/M_n = 1.33$ ) using DMF as the eluent; and <sup>1</sup>H NMR spectra (B) of PDMAEMA<sub>101</sub> and PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> in CDCl<sub>3</sub>.



**Figure S2.** FTIR spectrum of PEMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub>.



Figure S3. <sup>13</sup>C NMR spectrum of PEMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> in CDCl<sub>3</sub>.



**Figure S4.** TEM images of the mixed micellar aggregates of PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>83</sub> (1.0 mg/mL initial concentration of copolymer in DMF, and HAc/NaAc buffer solution content was 80% (wt%)), including sphere micelles, colloidal particles and aggregated hollow-sphere colloidal particles.



**Figure S5.** The optimized configurations of *cis*- and *trans*-isomers of hypothetical *linear*-azobenzene; (a) *cis* isomer of hypothetical *linear*-azobenzene; (b) *trans* isomer of hypothetical *linear*-azobenzene.



**Figure S6.** (A) and (B): The UV-vis absorption spectra of PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> in THF (0.05 mg/mL) under 365 nm light irradiation (35  $\mu$ W/cm<sup>2</sup>) and after the sample was placed in the dark at room temperature at different time intervals until the photo-stationary states were achieved; (C) and (D): The UV-vis absorption spectra of the micelles of PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> in HAc/NaAc buffer solution (1.0 mg/mL initial concentrations of block copolymer in DMF and buffer solution content was 80% (wt%) ) under 365 nm light irradiation (35  $\mu$ W/cm<sup>2</sup>) and after the sample was placed in the dark at room temperature at different time intervals until the photo-stationary states were achieved.



**Figure S7.** First-order kinetics for *trans-to-cis* and *cis-to-trans* photoisomerization corresponding to the absorbance at 345 nm of PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> in Figure S7. (A) and (B): PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> in THF (0.05 mg/mL); (C) and (D): PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> in HAc/NaAc buffer solution.



**Figure S8** (A) Fluorescence emission spectra upon adding different amount of HAc/NaAc aqueous solution into DMF solution of PDMAEMA<sub>101</sub>-*b*-PcyclicAzo<sub>31</sub> (initial concentration: 1.0 mg/mL); (B) TEM image of the copolymers solution when HAc/NaAc aqueous solution was added to 1600% (v/v) (( $V_{DMF}$ : $V_{buffer}$  = 1:16).

**Table S1.** The number-average molecular weight  $(M_n)$ , molecular weight distribution  $(M_w/M_n)$ and repeated DMAEMA units (m) and cyclicAzo units (n) of the PDMAEMA<sub>m</sub>-b-PcyclicAzo<sub>n</sub>

Sample	m	n	$M_{n,\rm NMR}$	M <sub>n,GPC</sub>	$M_{ m w}/M_{ m n}$
			(g/mol)	(g/mol)	
PDMAEMA <sub>101</sub> -b-PcyclicAzo <sub>31</sub> <sup>a</sup>	101	31	36900	22000	1.32
PDMAEMA <sub>101</sub> - <i>b</i> -PcyclicAzo <sub>83</sub> <sup>b</sup>	101	83	72100	33500	1.33

Feed molar ratio:

(a)  $[cyclicAzo]_0:[PDMAEMA]_0:[AIBN]_0 = 50:1:1;$ 

#### (b) $[cyclicAzo]_0:[PDMAEMA]_0:[AIBN]_0 = 200:1:1$

The dipole moments of *cis*- and *trans*-isomers of the *cyclic*-azobenzene pendants of the hydrophobic block as well as hypothetical *linear*-azobenzene were calculated at the B3LYP/6-31G(d) level with Gaussian 03.<sup>[S2]</sup>

 Table S2. Dipole moment components of the four stable conformations and total

 dipole moment

	$\mu_{\rm x}$	$\mu_{y}$	$\mu_z$	μ (total) <sup>a</sup>
cis-cyclic	-1.061 D	3.405 D	1.802 D	3.996 D
tran-cyclic	-3.192 D	-1.843 D	3.854 D	5.333 D
cis-linear	-1.977 D	3.268 D	2.839 D	4.759 D
tran-linear	-4.543 D	1.174 D	0.739 D	4.750 D

a: The total dipole moment was taken as the average over the four conformations and computed according to the following formula:

$$\overline{\mu} = \sqrt{\left(\overline{\sum_{conf} \overline{\mu}_x}\right)^2 + \left(\overline{\sum_{conf} \overline{\mu}_y}\right)^2 + \left(\overline{\sum_{conf} \overline{\mu}_z}\right)^2}$$

### **References:**

- [S1] X. Miao, J. Li, Z. Zhang, Z. Chen, W. Zhang, J. Zhu and X. Zhu, Polym. Chem., 2014, 5, 4641-4648.
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