Supporting Information for

A new visible light and temperature responsive diblock copolymer

Sijia Qian[a], Shenzhen Li,[a] Weifeng Xiong,*[,b] Habib Khan,[a] Jing Huang*[,c] and Wangqing Zhang*[,a,d]

[a] Key Laboratory of Functional Polymer Materials of the Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China. E-mail: wqzhang@nankai.edu.cn.

[b] State Key Laboratory of Special Functional Waterproof Materials, Beijing Oriental Yuhong Waterproof Technology Co., Ltd, Beijing 100123, China. E-mail: xiongwf@yuhong.com.cn.

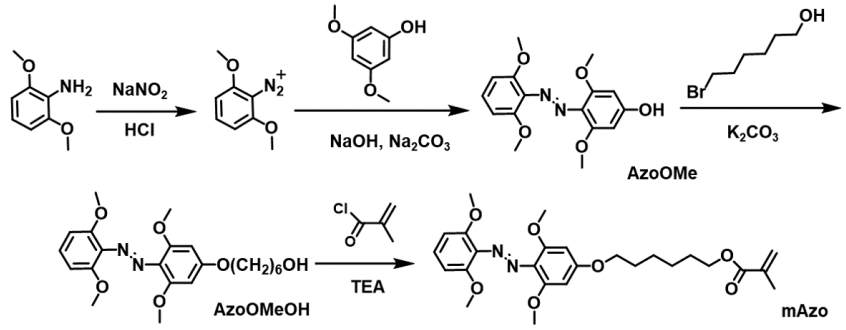
[c] Sinopec Research Institute of Petroleum Engineering, Beijing, China. E-mail: eleven413@126.com.

[d] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China.

*To whom correspondence should be addressed. Tel: 86-22-23509794, Fax: 86-22-23503510.

1. Synthesis of the mAzo monomer

The synthetic route of the monomer, 6-(2,6,2'6'-tetramethoxy-4'-oxyazobenzene) hexyl methacrylate (mAzo) is shown in Scheme S1.



Scheme S1. Synthetic route of mAzo monomer.

Synthesis of 4-(2,6-Dimethoxyphenyl) diazenyl)-3,5-dimethoxyphenol (AzoOMe).

2,6-Dimethoxyaniline (11.12 g, 0.073 mol) was dissolved in hydrochloric acid (30mL, 10%). The resulting solution was stirred for half an hour at room temperature and then cooled to 0 ^{o}C. Sodium nitrite (5.016 g, 0.073 mol), dissolved in cooled deionized water (70 mL), was slowly added to the former solution. After a clear solution of the diazonium salt was stirred for half an hour, 3,5-dimethoxyphenol (11.96 g, 0.073 mol) together with

sodium hydroxide (5.56 g, 0.1391 mol) dissolved in 300 mL water was slowly added to the resulting mixture at 0 ^{o}C. The pH of the mixture solution was maintained at 9 by adding sodium carbonate (10 g, 80 mL H_2O) and vigorously stirred at 0 ^{o}C for 1 h and then at room temperature for 3 days. The solution was acidified to pH 6 and stirred for an additional 30 min. Then the precipitated product was cooled with ice filtered, washed with ice cold water (100 mL) and purified by column chromatography (silica gel, ethyl acetate/ mineral ether (7/1), R_f =0.2) to receive the product as a red powder. Yield: 87%. ^{1}H NMR (400 MHz, DMSO, δ): 7.32 (t, J=8.4 Hz, 1H, Ar-H), 6.84 (d, J=8.8 Hz, 2H, Ar-H), 6.12 (d, J=2.4, 1H, Ar-H), 6.02 (s, J=2.4, 1H, Ar-H), 3.86 (s, 3H, O-CH_3), 3.83 (s, 3H, O-CH_3), 3.81 (s, 6H, O-CH_3). See ^{1}H NMR spectra in Figure S1.

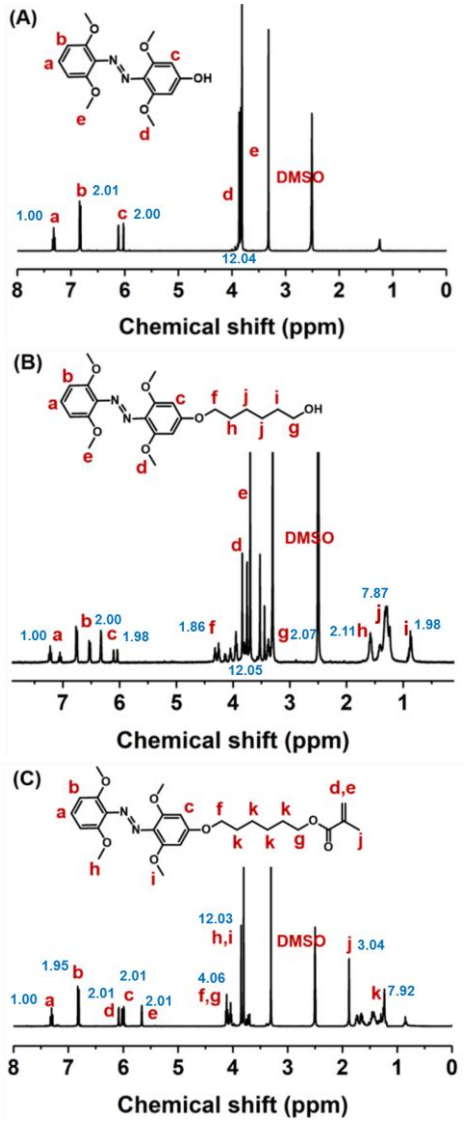


Figure S1. ^{1}H NMR spectra (400 MHz, DMSO-d6) of the mAzo monomer and its precursors.

Synthesis of 2,6,2',6'-Tetramethoxy-(4-(6-hydroxyhexyloxy)) azobenzene (AzoOMeOH).

AzoOMe (4.44 g, 14.15 mmol), anhydrous potassium carbonate (1.95 g, 14.15 mmol) and sodium iodide (0.212g, 4.245 mmol) were dissolved in dry DMF (70 mL). The resulting mixture was stirred for half an hour at 110 ^{o}C under an argon atmosphere. Diluent 6-bromo-1-hexanol (3.84 g, 21.23 mmol) was added dropwise and then stirred for 24h. The completion of the reaction was checked by thin layer chromatography using ethyl acetate as eluant. The red product was extracted with ethyl acetate and evaporated under reduced pressure and further purified using column chromatography (silica gel, ethyl acetate/mineral ether (5/1), R_f =0.2). Yield: 48%. ^{1}H NMR (400 MHz, DMSO, d): 7.05-7.23 (d, J=7.6Hz, 1H, Ar-H), 6.54-6,77 (t, J=8.4Hz, 2H, Ar-H), 6.11-6.32 (t, J=8.4Hz, 2H, Ar-H), 3.96- 4.32 (t, J=6.0Hz, 2H, Ar-O-CH_2), 3.84 (s, 3H, O-CH_3), 3.76 (s, 3H, O-CH_3), 3.70 (s, 6H, O-CH_3), 3.36-3.39 (t, J=5.6Hz, 2H, HO-CH_2), 0.88-1.58 (m, 8H, C-CH_2-C). See ^{1}H NMR spectra in Figure S1.

Synthesis of 6-(4-((2,6-Dimethoxyphenyl) diazenyl)- 3,5-dimethoxyphenoxy) hexyl methacrylate (mAzo).

AzoOMeOH (2.37 g, 5.68 mmol) and TEA (1.725 g, 17.04 mmol) were dissolved in CH_2Cl_2 (70 mL) and cooled to 0 ℃ under an argon atmosphere. Methacryloyl chloride (1.782 g, 17.04 mmol) was subsequently added dropwise under stirring. After 12 h, 5 mL ethanol was added and the solvent was removed under reduced pressure. The product was finally purified by column chromatography (silica gel, ethyl acetate / mineral ether (5/1), R_f = 0.2) Yield: 93%. ^{1}H NMR (400 MHz, DMSO, δ): 7.31 (t, J=8.4Hz, 1H, Ar-H), 6.83 (d, J=8.4Hz, 2H, Ar-H), 6.08 (d, J=2.4Hz, 2H, Ar-H), 6.02 (s, 1H, C=CH_2), 5.66 (m, 1H, C=CH_2), 4.17 (t, J=6.8Hz, 2H, Ar-O-CH_2), 4.02 (t, J=6.4Hz, 2H, O-CH_2), 3.88 (s, 6H, O-CH_3), 3.84 (s, 6H, O-CH_3), 1.88 (m, 3H, CH_3), 1.23-1.74 (m, 8H, -CH_2-CH_2-CH_2-CH_2-). See ^{1}H NMR spectra in Figure S1.

2. Equation

$$M_{n,th} = \frac{[\text{monomer}]_o \times M_{\text{monomer}}}{[\text{RAFT}]_o} \times conversion + M_{\text{RAFT}} \qquad \text{(S1)}$$

3. Polymerizations

Table S1. Conditions for the RAFT polymerization of mAzo.

NO.	$[mAzo]_0$:$[DDMAT]_0$:$[I]_0$	Time (h)	Conv.[a] (%)
1	80:1:1	15	28.8
2	80:1:1	24	42.3
3	80:1:1	39	48.8
4	240:3:1	12	12.1
5	240:3:1	24	17.1
6	240:3:1	39	19.9
9	400:5:1	24	10.6
10	400:5:1	44	16.1

Table S2. Summary of the effect of CTAs and solvents on the synthesis of PmAzo and PmAzo-*b*-PNIPAM.

NO.	monomers	[CTA]	Solvents	Time (h)	Conv.[a] (%)
1	mAzo	DDMAT	acetonitrile	15	28.8
2	mAzo	DDMAT	acetonitrile	24	46.1
3	mAzo	DDMAT	1,4-dioxane	15	18.3
4	mAzo	DDMAT	1,4-dioxane	24	27.1
5	mAzo	CDTPA	acetonitrile	15	25.7
6	mAzo	CDTPA	acetonitrile	24	45.2
7	mAzo	CDTPA	1,4-dioxane	15	17.7
8	mAzo	CDTPA	1,4-dioxane	24	26.0

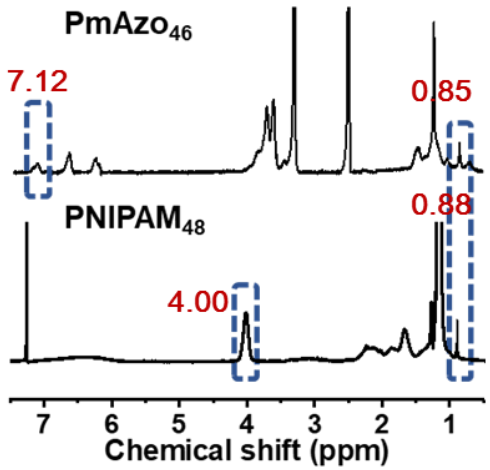


Figure S2. ^{1}H NMR spectra (400 MHz, DMSO-d6) of the $PmAzo_{46}$ and $PNIPAM_{48}$ macro-CTAs.

3. Thermo-response of the PmAzo-*b*-PNIPAM micelles

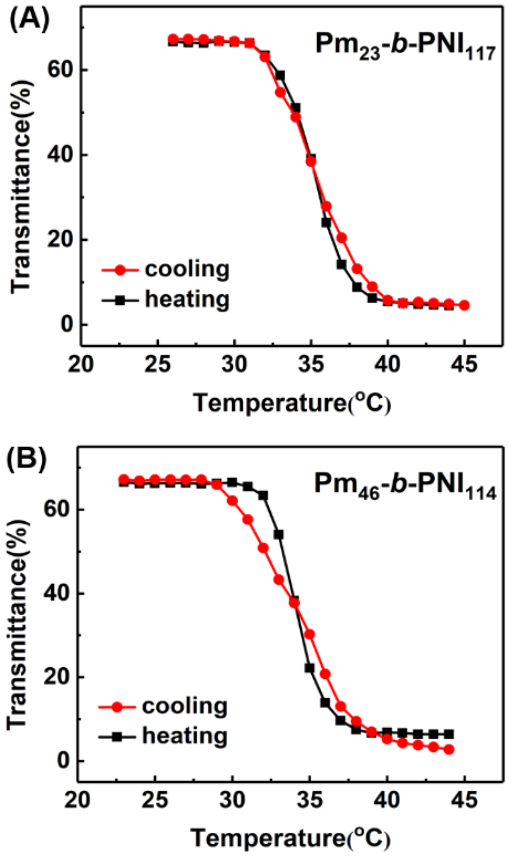


Figure S3. Temperature dependent transmittance of 0.1 mg mL^{-1} $PmAzo_{23}$-*b*-$PNIPAM_{117}$ and $PmAzo_{46}$-*b*-$PNIPAM_{114}$ micelles at 700 nm upon repeated cycles of heating/cooling.

4. DLS analysis

Table S3. Summary of DLS analysis of the PmAzo-*b*-PNIPAM micelles in water at 25 ℃.

sample	D_h (nm)	polydispersity	conc.(mg mL^{-1})
Pm_8-*b*-PNI_{112}	225±4	0.178	0.1
Pm_{23}-*b*-PNI_{117}	258±5	0.238	0.1
Pm_{46}-*b*-PNI_{114}	278±5	0.264	0.1
Pm_{74}-*b*-PNI_{110}	317±10	0.289	0.1
Pm_{46}-*b*-PNI_{90}	301±6	0.235	0.1
Pm_{46}-*b*-PNI_{50}	319±7	0.298	0.1

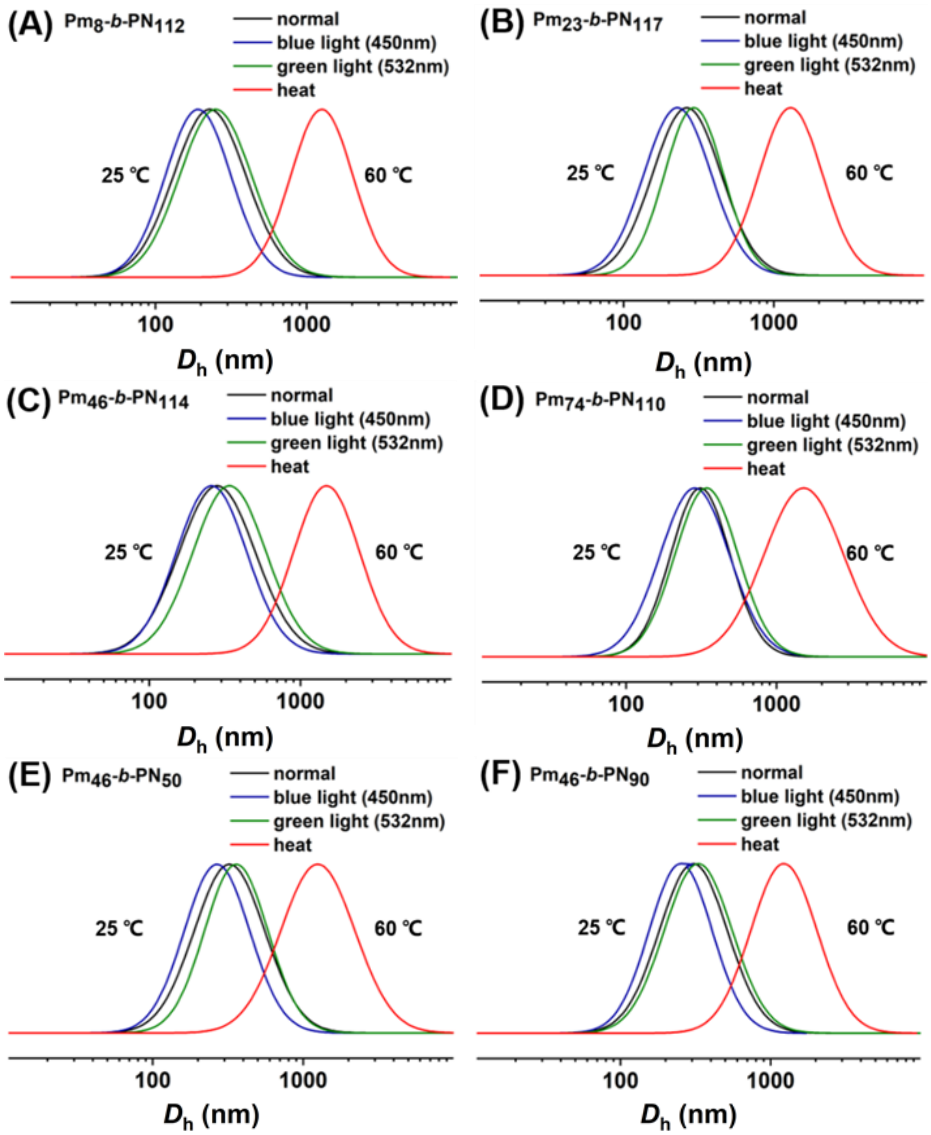


Figure S4. DLS analysis of 0.1 mg mL^{-1} block copolymer micelles: Pm_8-*b*-PNI_{112} (A), Pm_{23}-*b*-PNI_{117} (B), Pm_{46}-*b*-PNI_{114} (C), Pm_{74}-*b*-PNI_{110} (D), Pm_{46}-*b*-PNI_{50} (E) and Pm_{46}-*b*-PNI_{90} (F) with a given light irradiation at a temperature of 25 ℃ and 60 ℃.

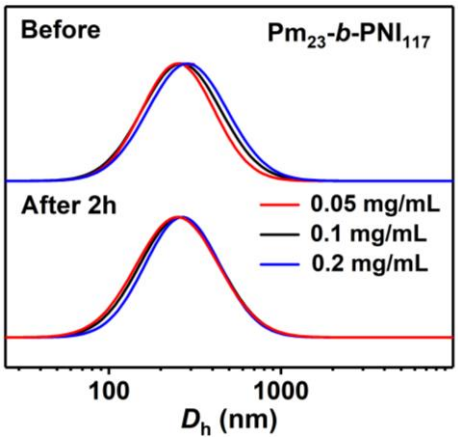


Figure S5. DLS analysis of the Pm_{23}-*b*-PNI_{117} micelles before and after diluting with water after 2 h at 25 ℃.

5. UV-vis analysis

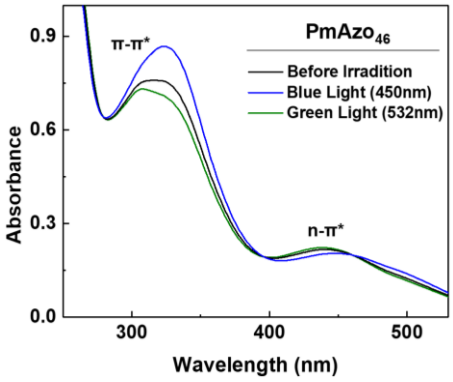


Figure S6. UV-Vis spectra of $PmAzo_{46}$ in DMF (0.1 mg mL^{-1}) under the irradiation of 532 nm green light and 450 nm blue light.

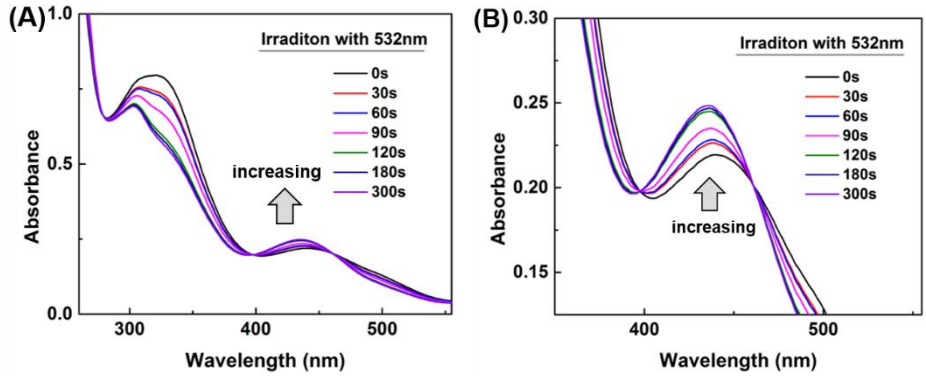


Figure S7. UV-Vis spectra of 0.1 mg mL^{-1} Pm_{23}-*b*-PNI_{117} micelles under the irradiation of 532 nm green light.

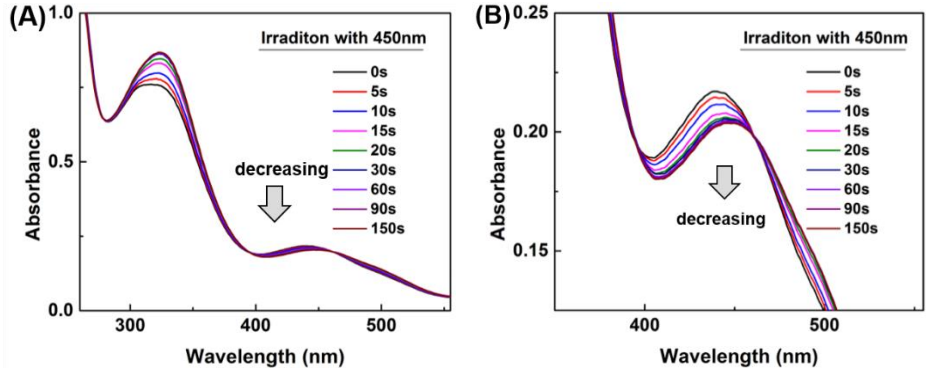


Figure S8. UV-Vis spectra of 0.1 mg mL^{-1} Pm_{23}-*b*-PNI_{117} micelles under the irradiation of 450 nm blue light.

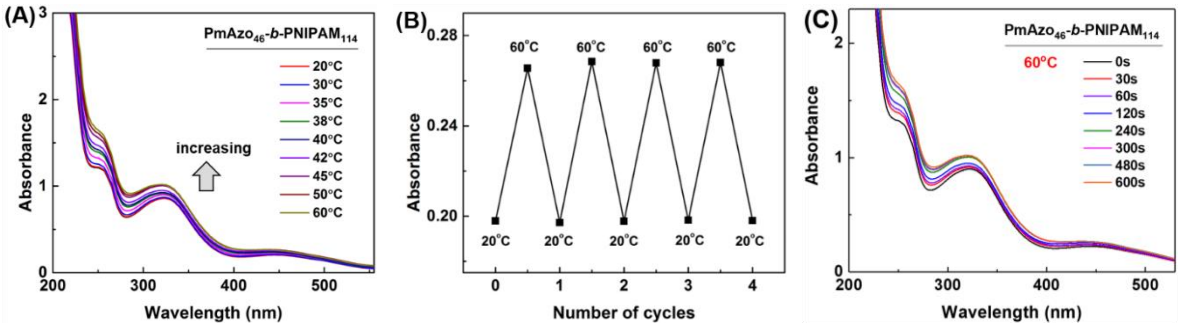


Figure S9. (A) UV-Vis spectrum of the 0.1 mg mL^{-1} Pm_{46}-*b*-PNI_{114} micelles gradually heating to 60 ℃ (B) The reversible absorbance changes at 438 nm heating to 60 ℃ and cooling down to 25 ℃. Note: in each temperature, the sample was initially kept for 5 min and then the absorbance is recorded. (C) UV-Vis spectra of the 0.1 mg mL^{-1} Pm_{46}-*b*-PNI_{114} aqueous dispersion in 60 ℃ under the irradiation of 450 nm blue light.

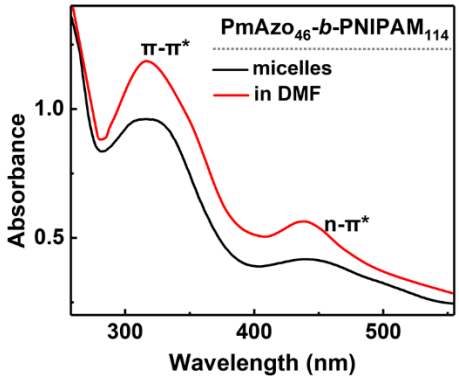


Figure S10. UV-Vis spectra of 0.1 mg mL^{-1} Pm_{46}-*b*-PNI_{114} block copolymer micelles dispersed in water and the DMF solution with the same polymer concentration.