# **Supporting Information for**

Synthesis and characterization of a novel azobenzene-containing polymer both in main- and side-chain with the unique photocontrolled isomerization property

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# **Experimental Section**

#### Synthesis



**Scheme S1.** Synthetic routes of 9,9'-dioctyl-2,7-dibromofluorene (DBF) and 9,9-di(4-methoxyazobenzene-4'-oxy)octyl-2,7-dibromofluorene (DBF-Azo).

#### Synthesis of 4'-methoxyl (4-hydroxy) azobenzene (Azo)

*P*-methoxyaniline (6.16 g, 50 mmol) was added to a solution of concentrated HCl (50.0%, 15 mL) in deionized water 45 mL. Then, a water solution (15 mL) of sodium nitrite (3.5 g, 50.7 mmol) was added slowly within 1 h. A yellow transparent diazonium salt solution was obtained. Meanwhile, a coupling solution was prepared as follows: phenol (8.00 g, 85.0 mmol), NaOH (4.00 g, 100 mmol), and NaHCO<sub>3</sub> (4.20 g, 50.0 mmol) were dissolved in 250 mL of water under vigorous stirring at 0-5 °C. Then the diazonium salt solution was added dropwise to the coupling solution within 20 min at 0-5 °C. The final mixture was reacted at 0-5 °C for 2 h. The precipitate was collected by filtration, washed with deionized water three times, and dried under vacuum. Compound 1 was then obtained. Red-orange crystal, yield 10.40 g, yield 91%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.89-7.85 (m, 4 H), 7.02-7.0 (d, 2 H), 6.94-6.91 (d, 2 H), 3.88 (s, 3 H), 5.0 (s, 1 H).

# Synthesis of 1-bromo-8-(4-methoxyazobenzene-4'-oxy) octane (BO-Azo)

Into a 500 mL single-neck, round-bottomed flask were placed (9.12 g, 0.04 mol) of 4'methoxyl (4-hydroxy) azobenzene and (10.88 g, 0.04 mol) of 1,8-dibromooctane, (0.29 mol, 40 g) of powdered potassium carbonate and 160 mL of acetone. The reaction mixture was refluxed for 20 h and then cooled and filtered to remove potassium bromide and excess potassium carbonate. The acetone was partially removed using a rotary evaporator, and the reaction mixture was cooled to induce crystallization. The crystalline product was filtered and washed thoroughly with *n*-hexane. After recrystallization from absolute ethyl acetate or a mixture of dichloromethane and methanol, the product was dried in a vacuum oven. Yellow powder, yield 11.9 g, yield 71.2%. <sup>1</sup>H-NMR (CDCl3),  $\delta$  (TMS, ppm): 7.94-7.83 (m, 4 H), 7.05-6.94 (d, 4 H), 4.08-3.97 (d, 2 H), 3.93-3.83 (s, 3 H), 3.46-3.36 (s, 2 H), 1.94-1.73 (d, 4 H), 1.56-1.28 (d, 8 H).

# Synthesis of 9, 9'-dioctyl-2,7-dibromofluorene (DBF)

To a stirred solution of 1-bromooctane (5.86 mL, 33.7 mmol) and 2,7-dibromo-9*H*-fluorene(3.67 g, 13.48 mmol) in dimethyl sulfoxide (40 mL) was added sodium hydroxide powder (3.55 g, 22.7 88.7 mmol) rapidly at room temperature and then temperature was heated to 56 °C. The solution was stirred for 36 h at 60 °C. The product was diluted in 200 mL of ethyl acetate. After filtration, the product was extracted with salt brine and washed with water, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The product was recrystallized from a mixture of dichloromethane and methanol to give a solid (5.61 g, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.62–7.28 (6 H, m), 1.89–1.76 (4 H, d), 1.27–0.89 (20 H, dd), 0.81–0.70 (6 H, m), 0.58–0.40 (4 H, m).

# Synthesis of 9,9-di(4-methoxyazobenzene-4'-oxy)octyl-2,7-dibromofluorene (DBF-Azo)

To a stirred solution of 1-bromo-8-(4-methoxyazobenzene-4'-oxy)octane (2.09 g, 5.0 mmol) and 2,7-dibromo-9*H*-fluorene(0.74 g, 2.9 mmol) in dimethyl sulfoxide (40 mL) was added sodium hydroxide powder (0.91 g, 22.7 mmol) rapidly at room temperature and then temperature was heated to 56 °C. The solution was stirred for 36 h at 60 °C. The product was diluted in 200 mL of ethyl acetate. After filtration, the product was extracted with salt brine and washed with water, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The product was recrystallized from a mixture of dichloromethane and methanol to give a yellow solid (2.97 g, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.92–7.82 (8 H, ss), 7.57–7.41 (6 H, d),7.04–6.91 (8 H, dd), 4.05–3.93 (4 H, m), 3.91–3.86 (6 H, m), 1.97–1.86 (4 H, m), 1.80–1.66 (4 H, m),

1.48–1.00 (16 H, m), 0.67–0.52 (4 H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 161.53, 161.21, 152.49, 147.10, 146.89, 139.07, 130.22, 126.17, 124.34, 121.52, 121.20, 114.68, 114.17, 68.27, 55.69, 55.56, 40.14, 31.61, 29.74, 29.21, 29.13, 29.08, 25.89, 25.61, 22.68.



**Fig. S1** <sup>1</sup>H NMR spectrum of 9,9-di(4-methoxyazobenzene-4'-oxy)octyl-2,7-dibromofluorene in CDCl<sub>3</sub>.



**Fig. S2** <sup>13</sup>C NMR spectrum of 9,9-di(4-methoxyazobenzene-4'-oxy)octyl-2,7-dibromofluorene in CDCl<sub>3</sub>.





### Synthesis of 4,4'-dihydroxyazobenzene ditriflate (DT-Azo)

4,4'-Dihydroxyazobenzene (4.3 g, 20 mmol) and 20 mL of pyridine were stirred in a 100 mL flask placed in an ice bath at 0 °C. Then triflic anhydride (16.9 g, 60 mmol) was added dropwise and the mixture kept at 0 °C for 5 minutes before warming to room temperature. After 4.5 h, the mixture was poured into 100 mL of H<sub>2</sub>O, extracted with diethyl ether. The organic layer was washed with H<sub>2</sub>O, 10% HCl and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. Column chromatography (petroleum ether/EtOAc, 10:1, v/v) gave an orange powder (8.1 g, 84.7%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.15-8.01 (d,4 H), 7.87-7.68 (d,4 H).

#### Synthesis of azobenzene-4,4'-diboronic ester (DE-Azo)

A solution of 4,4'-dihydroxyazobenzene ditriflate (4.78 g, 10 mmol), bis(pinacolato)diboron (6.35 g, 25 mmol), KOAc (5.88 g, 60 mmol), and dppf (0.33 g, 0.6 mmol) in degassed 1,4-dioxane (50 mL) was stirred under argon atmosphere. Then  $PdCl_2(dppf) \cdot CH_2Cl_2$  (0.48 g, 0.6 mmol) was added under argon atmosphere and the reaction was heated to 80 °C for 12 h. The reaction was diluted with EtOAc (100 mL), filtered through Celite, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was washed with petroleum ether by ultrasonic washer to afford an orange powder (2.61 g, 60.1%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.02-7.96 (d, 4 H), 7.95-7.89 (d, 4 H), 1.40 (s, 24 H).



Fig. S3 <sup>1</sup>H NMR spectra of AzoF8 in CDCl<sub>3</sub>.



Fig. S4 <sup>1</sup>H NMR spectra of AzoF8-alt-Azo in CDCl<sub>3</sub>.



**Fig. S6** Photoisomerization switching of the UV-vis spectra of AzoF8 solution by alternating irradiation with 365 nm and 435 nm light. The irradiation times for 365 nm light and 435 nm light

are both 3 min. The absorbance change for *trans*- and *cis*-form is taken from 360 nm (black) and 450 nm (red), respectively. The concentration of polymer repeating unit is  $2.38 \times 10^{-5}$  mol/L.



Fig. S7 Changes in UV-vis spectra of AzoF8 in CHCl<sub>3</sub> under different irradiation times with 546 nm irradiation. [repeating unit]<sub>0</sub> =  $2.38 \times 10^{-5}$  mol L<sup>-1</sup>.



**Fig. S8** Changes in UV-vis spectra of F8-*alt*-Azo in CHCl<sub>3</sub> under different irradiation times with 365 nm, 435 nm and 546 nm light at 25 °C. (a) 365 nm irradiation, (b) 435 nm irradiation, (c) 546 nm irradiation and (d) magnified parts of (c). [repeating unit]<sub>0</sub> =  $3.87 \times 10^{-5}$  mol L<sup>-1</sup>.

The first-order rate constant  $k_e$  of *trans*-to-*cis* photoisomerization was determined by the Formula S1<sup>1,2</sup>:

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

Where  $A_{\infty}$ ,  $A_t$ , and  $A_0$  are absorbance at about 360 nm and 425 nm corresponded to the  $\pi$ - $\pi$ \* transition of *trans* isomers of *s*- and *m*-Azo at infinite time, time t and time zero with irradiation of different wavelength light (313 nm, 365 nm, 405 nm and 435 nm) at room temperature, respectively.

The first-order rate constant  $k_{\rm H}$  of *cis*-to-*trans* recovery was determined by the Formula S2<sup>1,2</sup>:

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

Where  $A_{\infty}$ ,  $A_t$ , and  $A_0$  are absorbance at about 360 nm and 425 nm corresponded to the  $\pi$ - $\pi$ \* transition of trans isomers of azobenzene at infinite time, time t and time zero with irradiation of different wavelength light (435 nm and 546 nm) at room temperature, respectively.

The first-order kinetic curves of photoisomerization are plotted in Fig. 4 and Fig. S9.



Fig. S9 Changes in UV-vis spectra of AzoF8 in CHCl<sub>3</sub> under different irradiation times with 313 nm, 405 nm, 435 nm and 546 nm light at 25 °C. (a) 313 nm light; (b) 405 nm light; (c) 435 nm light; (d) 546 nm light. [repeating unit]<sub>0</sub> =  $2.38 \times 10^{-5}$  mol L<sup>-1</sup>.



**Fig. S10** Changes in UV-vis spectra of F8-*alt*-Azo in CHCl<sub>3</sub> under different irradiation times with 313 nm, 405nm, 435 nm and 546 nm light at 25 °C. (a) 313 nm light; (b) 405 nm light; (c) 435 nm light; (d) 546 nm light; (e) are magnified parts of (b). [repeating unit]<sub>0</sub> =  $3.87 \times 10^{-5}$  mol L<sup>-1</sup>.



**Fig. S11** First-order kinetics for reversible photoisomerization of AzoF8-*alt*-Azo. (a) The *trans-cis* photoisomerization rate constants of *s*-Azo via 313 nm irradiation, (b) The *trans-cis* photoisomerization rate constants of *s*-Azo via 405 nm irradiation, (c) The total photoisomerization rate constants of both side-chain and *m*-Azo via 405 nm irradiation, (d) The *cis-trans* photoisomerization rate constants of side-chain Azo via 435 nm irradiation, (e) The *cis-trans* photoisomerization rate constants of main-chain Azo via 546 nm irradiation.

Entry	λ/nm	λ <sub>irradiation</sub>	s-Azo		<i>m</i> -Azo	
		/nm	$k_{\rm e}/{\rm s}^{-1}$	$k_{ m H}/ m s^{-1}$	$k_{\rm e}/{\rm s}^{-1}$	$k_{ m H}/{ m s}^{-1}$
1	360	313	0.0231	-	-	-
2	360	405	0.0321	-	-	-
	450		-	-	0.1111	-
3	360	435	-	0.0290	-	-
4	520	546	-	-	-	0.00525

Table S1 Photoisomerization rate of AzoF8-alt-Azo.



**Fig. S12** Changes in UV-Vis spectra of AzoF8-*alt*-Azo in CHCl<sub>3</sub> under 365 nm light irradiation (a) and heating relaxation (b). The plots of *cis*-to-*trans* thermal back-isomerization (c) and the data come from (b). [repeating unit]<sub>0</sub> =  $2.45 \times 10^{-5}$  mol L<sup>-1</sup>.



**Fig. S13** Changes in UV-Vis spectra of AzoF8-*alt*-Azo in CHCl<sub>3</sub> under 365 nm light irradiation (a), 435 nm light irradiation (b) and heating relaxation (c). (d) is the plots of *cis*-to-*trans* thermal back-isomerization and the data come from (c). [repeating unit]<sub>0</sub> =  $1.88 \times 10^{-5}$  mol L<sup>-1</sup>.

- 1. T. García, L. Larios-López, R. J. Rodríguez-González, G. Martínez-Ponce, C. Solano and D. Navarro-Rodríguez, *Polymer*, 2012, **53**, 2049-2061.
- 2. X. Jiang, J. Lu, F. Zhou, Z. Zhang, X. Pan, W. Zhang, Y. Wang, N. Zhou and X. Zhu, *Polym. Chem.*, 2016, **7**, 2645-2651.