

Supporting Information

Reversible Photo-controlled Mass Transfer in Photo-responsive Conjugated Main-chain Polymer Film for Highly Contrast Surface Patterning

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1. Synthesis of polymer PFazo

M1. 2,7-dibromo-9H-fluorene. To a solution of 6 g (36 mmol) 9H-fluorene, 92 mg (1.6 mmol) iron (III) chloride in CH₂Cl₂ (100 mL) at 0 °C, 4 mL bromine was added drop by drop. The mixture was stirred at 0 °C for 12 hours, avoided from sunlight. The mixture was poured into 50 mL water, and then organic layer was extracted with CH₂Cl₂ for several times. The organic phase was dried over anhydrous magnesium sulphate. After filtration the solvent was removed using rotary evaporation, and the residue was recrystallized in ethanol resulting white crystalline product (yield 75%). ¹H NMR (500 MHz, CDCl₃, ppm): δ7.66 (s, 2H, Ar-H), δ7.60-7.59 (d, 2H, Ar-H), δ7.51-7.49 (d, 2H, Ar-H), δ3.87 (s, 2H, Ar-H). MS (m/z) 323.9. Anal. Calcd. for C₁₃H₈Br₂: C 48.19, H 2.49; Found: C 48.54, H 2.51.

M2. 2,7-dibromo-9,9-dihexyl-9H-fluorene. 2.8 g (8.6 mmol) 2,7-dibromo-9H-fluorene, 0.29 g (0.86 mmol) TBABr and 2.8 mL (3.3 g, 20 mmol) 1-bromohexane were added into a rockered flask (100 mL) with 0.8 mL NaOH aqueous solution (40 mol L⁻¹) and 5 mL refined toluene. The mixture was refluxed at 110 °C for 24 hours. After cooled down to room temperature, the mixture was poured into 50 mL water and extracted it with CHCl₃ for three times. The organic phase was dried over anhydrous magnesium sulphate. After removing the solvent using rotary evaporation, the residue was purified by column chromatography (silica gel, hexane) to give a white solid (yield 72%). ¹H NMR (500 MHz, CDCl₃, ppm): δ7.53-7.51 (d, 2H, Ar-H), δ7.46-7.44 (m, 4H, Ar-H), δ1.91-1.89 (m, 4H, CH₂), δ1.13-1.04 (m, 12H, CH₂), δ0.79-0.77 (m, 6H, CH₃), δ0.58 (m, 4H, CH₂). MS (m/z) 492.4. Anal. Calcd. for C₂₅H₃₂Br₂: C 60.99, H 6.55; Found: C 61.23, H 6.47.

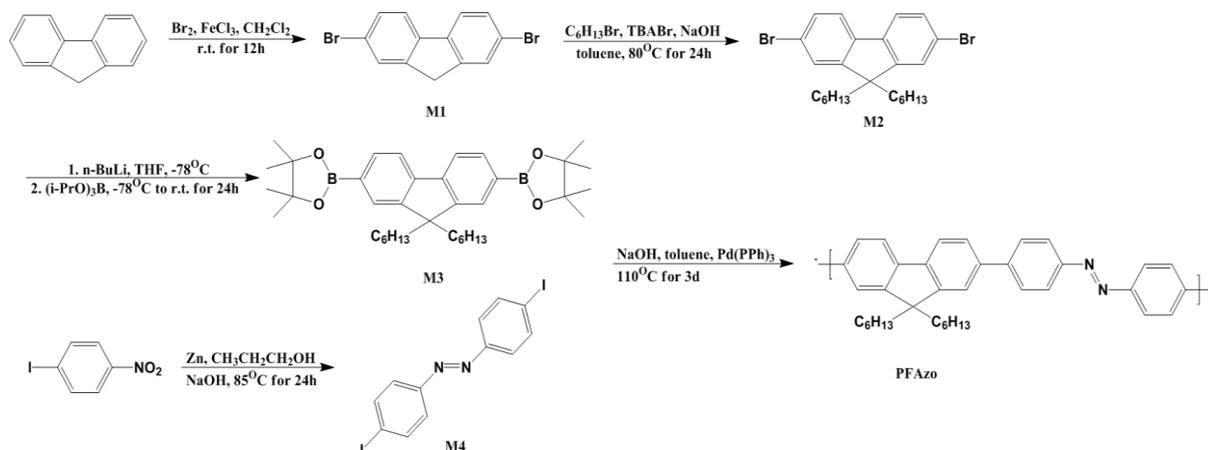
M3. 2-(9,9-dihexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 8 g (10 mmol) 2,7-dibromo-9,9-dihexyl-9H-fluorene was dissolved in refined THF(100 mL) and decrease the temperature to -78 °C. In the protection of N₂, 13 mL (22 mmol) *n*-butyllithium was added into the solution. The mixture was stirred at -78 °C for 2 hours, and then warmed to room temperature for 15 min. After

being cool again to $-78\text{ }^{\circ}\text{C}$ for 15 min, 7.9 mL (35 mmol) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added rapidly to the solution. About 2 hours later, the resulting mixture was warmed to room temperature and stirred for 48 hours. The mixture was poured into 50 mL water with stirring, and then the organic layer was extracted with CH_2Cl_2 for three times. The organic phase was dried over anhydrous magnesium sulphate. After being filtrated the solvent was removed using rotary evaporation, and the residue was purified by column chromatography (silica gel, CH_2Cl_2 and diethyl ether) to give a white solid. The solid was recrystallized in ethanol to give white crystalline product (yield 65%). ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.81-7.79 (d, 2H, Ar-H), δ 7.74-7.73 (d, 2H, Ar-H), δ 7.71 (s, 2H, Ar-H), δ 2.01-1.99 (m, 4H, CH_2), δ 1.39 (s, 24H, CH_3), δ 1.08-0.98 (m, 12H, Ar-H), δ 0.75-0.73 (m, 6H, CH_3), δ 0.55-0.54 (m, 4H, CH_2). MS (m/z) 586.5. Anal. Calcd. for $\text{C}_{37}\text{H}_{56}\text{B}_2\text{O}_4$: C 75.78, H 9.62; Found: C 75.50, H 9.86.

M4. 1,2-bis(4-iodophenyl)diazene. After 360 mg (9 mmol) sodium hydroxide was added into a 50 mL round-bottomed flask with 0.75 mL distilled water and 4 mL propanol, 288 mg (4.5 mmol) zinc dust and 500 mg (2.01 mmol) 1-iodo-4-nitrobenzene were added into the solution. The mixture was refluxed at $90\text{ }^{\circ}\text{C}$ for 24 hours, and filtered while hot, and then the precipitate of sodium zincate was washed on the filter with 50 mL warm methanol. The residue solution was added to 10 mL 2% hydrochloric acid, and then the mixture was warmed to about $70\text{ }^{\circ}\text{C}$ in order to melt the production and stirred rapidly for about 5 minutes. Stop heating but continue to stir till the mixture was chilled to solidify the 1,2-bis(4-iodophenyl)diazene. The product was filtered, washed well with distilled water, and recrystallized in a mixture of 7.2 mL ethanol and 0.6 mL water to get orange crystalline product (yield 35%). ^1H NMR (500 MHz, CDCl_3 , ppm): δ 7.96-7.91 (d, 8H, Ar-H). MS (m/z) 433.9. Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{I}_2\text{N}_2$: C 33.21, H 1.86, N 6.45; Found: C 33.18, H 1.75, N 6.53.

Synthesis of polymer PFAzo. 200 mg
2-(9,9-dihexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-7-yl)-4,4,5,5-tetra

methyl-1,3,2-dioxaborolane (M3), 148 mg 1,2-bis(4-iodophenyl)diazene (M4) and 14.7 mg Pd(PPh₃)₄ catalyzer were added into a 50 mL round-bottomed flask with 4.25 mL distilled DMAc. Then the solution of 54.4 mg NaOH in 0.68 mL water was dropped into the flask. The mixture was degassed twice by the freeze-pump-thaw procedure, followed by refluxed at 110 °C for 48 hours under nitrogen atmosphere. After cooled down to room temperature, the mixture was poured into 50 mL water with stirring, followed by extraction with CH₂Cl₂ for three times. The organic layer was dried over anhydrous MgSO₄, and after the solvent being removed using rotary evaporation, the residue was purified by Al₂O₃ column chromatography. The solution was concentrated and the desired polymer was precipitated from methanol and obtained yellow solid (yield 85%), Mw=39k (PD=1.27). ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.12-8.04 (m, 4H, Ar-H), δ 7.90-7.82 (m, 6H, Ar-H), δ 7.73-7.64 (m, 4H, Ar-H), δ 2.13-1.99 (m, 4H, CH₂), δ 1.20-1.03 (m, 12H, CH₂), δ 0.78-0.61 (m, 10H, CH₂). ¹³C NMR (125 MHz, CDCl₃, ppm): δ =151.87, 147.17, 144.84, 144.05, 143.14, 142.65, 140.82, 140.50, 139.12, 138.45, 127.72, 127.34, 126.30, 123.41, 122.78, 121.45, 120.29, 55.37, 40.33, 31.38, 29.60, 23.76, 22.49, 13.91. FT-IR (KBr pellets, cm⁻¹): 3314, 3041, 2926, 2847, 1605, 1456, 1248, 1228, 1152, 1008, 889, 852, 816, 740, 565, 525. Anal. Calcd. for (C₃₆H₄₀N₂)_n: C 86.67, H 7.86, N 5.46; Found: C 86.91, H 7.75, N 5.33.



Scheme S1. Synthesis route of conjugated polymer PFAzo by Suzuki coupling reaction.

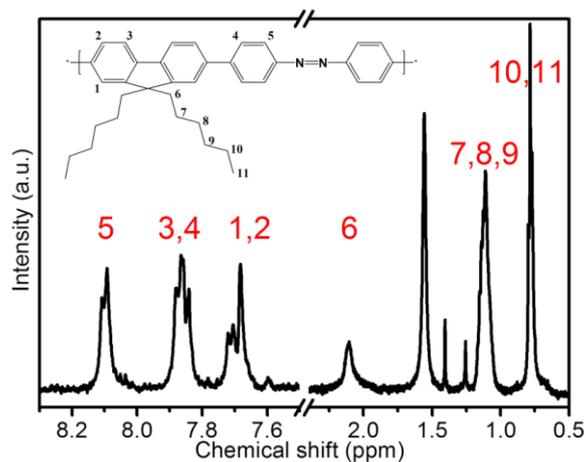


Figure S1. ¹H NMR (500 MHz) spectrum of PFAzo at room temperature by utilizing CDCl₃ as the solvent.

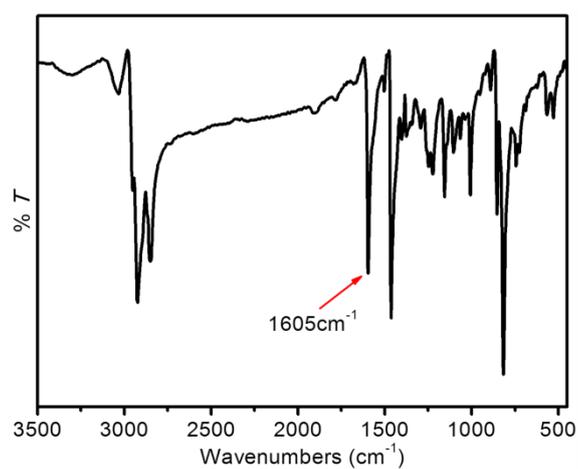


Figure S2. FT-IR spectrum of PFAzo at room temperature by KBr pellets, and the peak at 1605 cm⁻¹ belongs to Vs (N=N).

2. The thermal properties of the polymer PFAzo

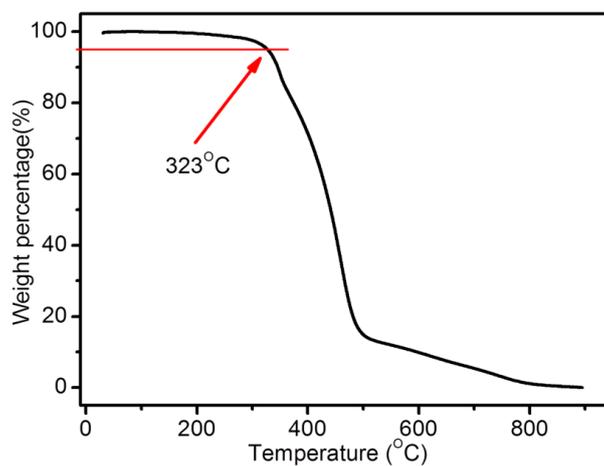


Figure S3. The TGA curve recorded at a heating rate 10 K/min, and the thermal decomposition is 323 °C.

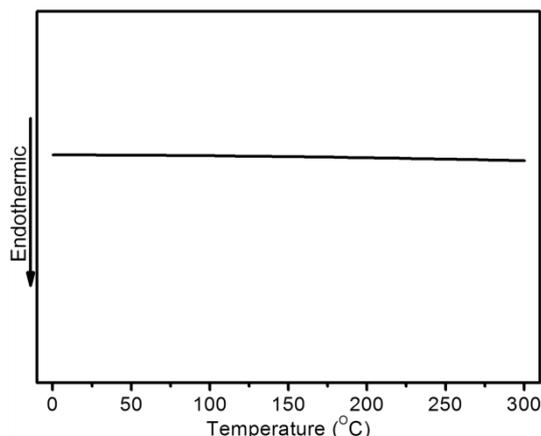


Figure S4. DSC data recorded at a heating rate 10 K/min, and there is no obviously Tg between 0-300 °C.

3. DFT computation for the length change of polymer chain

Molecular simulation was performed based on Density functional theory (DFT) as implemented in the Gaussian 03 program to optimize the chain structure *trans*- and *cis*-conformation of P1 (PFAzo with repeat units of 1). As shown in **Figure S5**, the chain length of *trans*- and *cis*-conformation of P1 is 19.69 Å and 15.52 Å respectively, and the change of chain length is 4.17 Å. Molecules with the repeat units of 2, 3, 4 were calculated by the same way, as shown in **Table S1**. Obviously depicted in the table is that the length of PFAzo with repeat units of 4 between *trans*- and *cis*-conformation is 24.95 Å, which is much larger than 4 times (16.68 Å) of repeat units of 1 (4.17 Å). Because the chain length of *trans*-conformation of the four molecules is almost linear-increased because of the all conjugated main chain, while the increase of *cis*-conformation is relatively slow because of its curly and helical conformation. We further speculated that the chain length of all *trans*-polymer (repeat units of 75) was 147.68 nm, and the chain length of PSS polymer (80% *cis*-content) was 123.28 nm using P1 as a primary standard for the maximum. According to the most conservative estimate, the length change of main chain is much more than 24.40 nm. So it is not difficult to understand why the surface modulation depth of PFAzo film is much

deeper than that of other materials, in which azobenzene moiety is not containing in main chain.

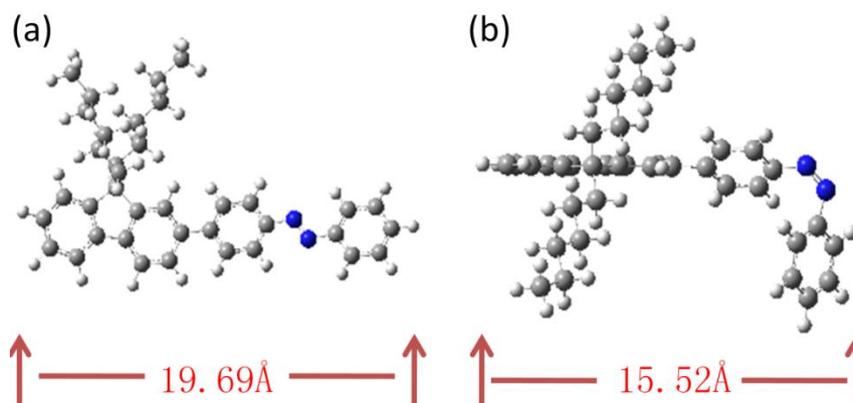


Figure S5. (a) The chain length of *trans*-conformation of P1 is 19.69 Å; (b) the chain length of *cis*-conformation of P1 is 15.52 Å, computed by DFT in Gaussian 03 program.

Table S1. The chain length of *trans*- and *cis*- conformation of PFAzo (n=1, 2, 3, 4)

| PFAzo | n=1 | n=2 | n=3 | n=4 |
|-------------------|-------|-------|-------|-------|
| <i>cis</i> /Å | 15.52 | 27.47 | 38.90 | 50.72 |
| <i>trans</i> /Å | 19.69 | 38.30 | 57.28 | 75.67 |
| Δ length/Å | 4.17 | 10.83 | 18.38 | 24.95 |

4. The AFM image of the cross-section of surface pattern

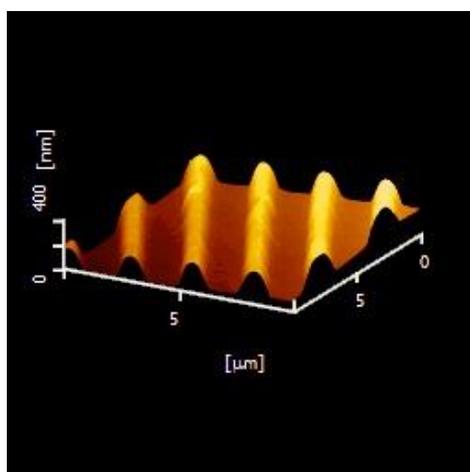


Figure S6. The AFM image of cross-section of PFAzo surface pattern irradiated by 355 nm interfering laser beam for 15 s (intensity of 40 mW cm^{-2} , grating spacing of $2.4 \mu\text{m}$), which shows the surface modulation depth of 290 nm (shown in **Figure 2c**).

5. UV-Vis and fluorescence spectra of *trans*- to *cis*- photoisomerization

The PFAzo film was irradiated by a 250 W lamp bulb with 355 nm wavelength, UV-Vis spectrum changed remarkably, as shown in **Figure 1**. Then the PFAzo at PSS can transform to the initial state irradiated by a 250 W lamp bulb, as shown in **Figure S7**. In the process of PFAzo *trans*- to *cis*- photoisomerization, UV-Vis spectrum changes hugely and rapidly, however, this kind of rapid change of fluorescence spectra was also discovered not only in PFAzo solution but also on films. The maximum wavelengths of the PL spectra are in the blue region near 450 nm and at the same time the fluorescence intensity became stronger and stronger with the increase of the content of *cis*-PFAzo (**Figure S8**). The photograph of the PFAzo solution irradiated by 355 nm wavelength light was shown in **Figure S9**. Luminescence intensity of solution with high *cis*-content PFAzo is strong enough to be observed, however luminescence of all *trans*-PFAzo is quenched absolutely.

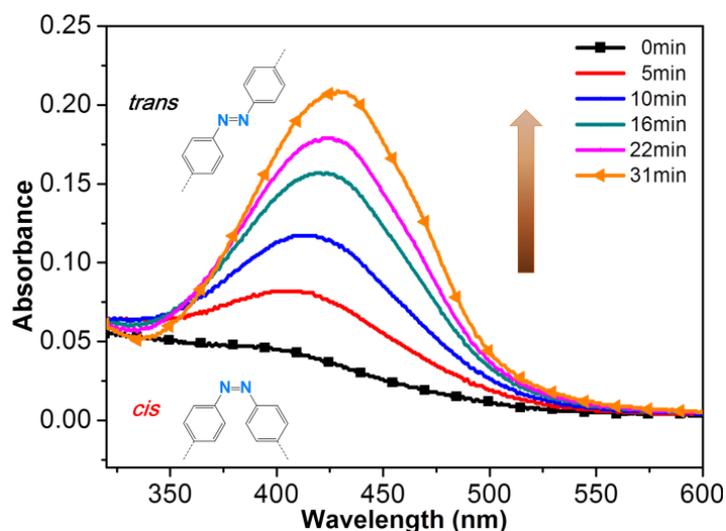


Figure S7. UV-Vis spectra of PFAzo film at PSS with different irradiated time by 480 nm light (intensity of 15 mW cm^{-2}). The solid black curve is the absorption spectrum of PFAzo

film at PSS before irradiation and the solid orange curve is the absorption spectrum after irradiation to the initial state (shown in **Figure 1**).

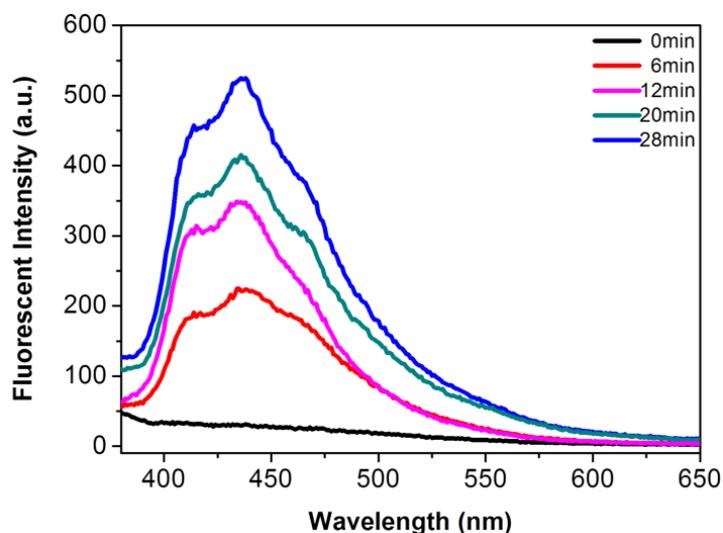


Figure S8. Fluorescent spectra of PFAzo film as different irradiation time with 355 nm light (intensity of 20 mW cm^{-2}). The solid black curve is the fluorescent spectrum of PFAzo film before irradiation and the solid blue curve is the fluorescent spectrum after irradiation to photo stationary state (PSS).

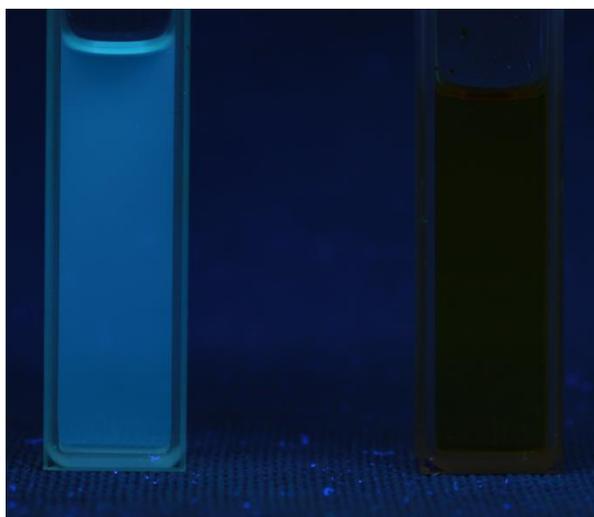


Figure S9. Image of the PFAzo solution irradiated by 355 nm light. Left: high *cis*- content PFAzo solution with observable blue fluorescence; Right: all *trans*-PFAzo solution with non-fluorescence.