Supplementary Information

Polymer Brush-Functionalized Surfaces with Unique Reversible Double-Stimulus Responsive Wettability

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S1. Synthesis of azo monomer.

Materials. 4-(Trifluoromethoxy)aniline (99%), 2-bromoethanol (96%), potassium iodide (KI, 99.9%), triethylamine (99.9%), 4-dimethylamiopryidine (DMAP, 98%) and methacryloyl chloride (95%) were purchased from Aladdin. Phenol (99%), sodium nitrite ($NaNO_2$, 99%), sodium carbonate (Na_2CO_3, 99%), sodium hydroxide (NaOH, 96%), concentrated sulfuric acid (98%), potassium carbonate (K_2CO_3, 99%), *N*,*N*-Dimethylformamide (DMF, 99.5%), dichloromethane (99.5%) and acetone (99.5%) were purchased from Sinopharm Chemical Reagent Corp.

Synthesis. Synthetic route for synthesis of azo monomer was shown in **Scheme S1**.

4-Hydroxy-4'-trifluoromethoxy-azobenzene (1)

(1) was synthesized according to a previously described method.[1] Typically, 0.075 mol of 4-trifluoromethoxy-aniline was dissolved under heating in a mixture of 21 ml concentrated sulphuric acid and 21 ml water. After that the solution was cooled to 0°C followed by dropwise addition of a solution of 0.1 mol $NaNO_2$ in 40 ml water at 0°C to start diazotization reaction. The mixture was stirred at 0-5 °C for 15 min. The coupling reaction was carried out by slowly adding the diazotization

solution to a solution of 0.08 mol phenol, 0.087 mol NaOH and 0.566 mol Na_2CO_3 in 360 ml water at 0-5 °C. The yellow-orange colored precipitate of (1) was filtered, dried and recrystallized from *n*-hexane.

^{1}H NMR (500 MHz, CDCl3, TMS) δ [ppm]: 6.96 (2H, d, Ar-H), 7.33 (2H, d, Ar-H), 7.91 (4H, t, Ar-H). GC-MS: 99.5%, m/z = 282.

4-(2-hydroxyethyloxy)-4'-trifluoromethoxy-azobenzenes (2)

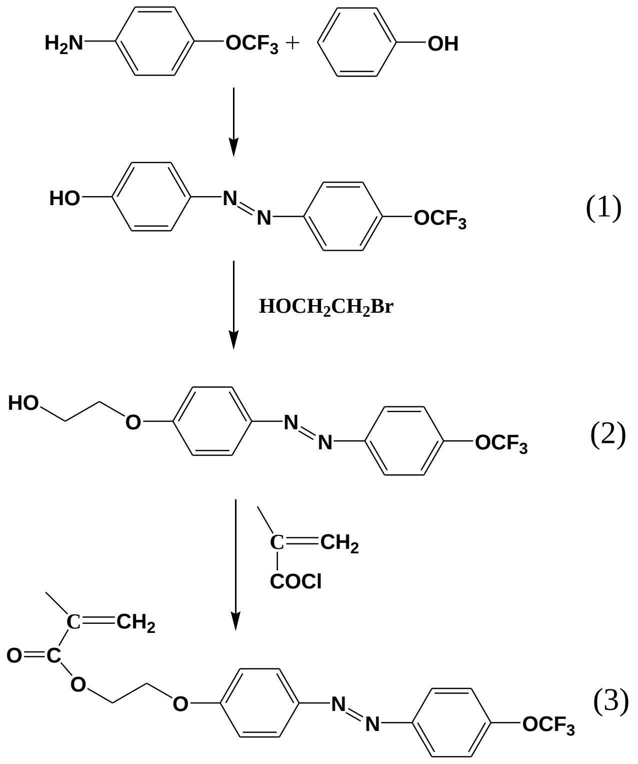
30 mmol of (1), 150 mmol of dry K_2CO_3 and a trace of KI were mixed in 120 ml dry acetone and heated to 50°C. After stirred for 0.5 h, 2-bromoethanol was added dropwise into the mixture. The mixture was then stirred vigorously and refluxed for 5 days. After cooled, the precipitated salt was filtered. The crude product was dissolved in dichloromethane and washed with water for 5 times to remove the unreacted 2-bromoethanol and salt.

^{1}H NMR (500 MHz, CDCl3, TMS) δ [ppm]: 4.02 (2H, t, CH_2O), 4.19 (2H, t, CH_2O), 7.04 (2H, d, Ar-H), 7.33 (2H, d, Ar-H), 7.91 (4H, t, Ar-H). GC-MS: 99.8%, m/z = 326.

[4-(2- methylacryloyloxy) ethyloxy-4'-trifluoromethoxy] azobenzenes (3)

5 mmol of (2), 10 mmol of triethylamine, 0.1 mmol of DMAP and 10 mmol of methacryloyl chloride was dissolved in dichloromethane, and stirred at 20 °C for 12 h. Then the solution was concentrated by distillation and purified by column chromatography using petroleum ether and ethyl acetate (volume ratio: 5:1) as the eluent.

^{1}H NMR (500 MHz, CDCl3, TMS) δ [ppm]: 1.96 (3H, s, CH), 4.32 (2H, t, CH_2O), 4.54 (2H, t, CH_2O), 5.61 (1H, s, CH2=), 6.16 (1H, s, CH2=), 7.02 (2H, d, Ar-H), 7.33 (2H, d, Ar-H), 7.91 (4H, t, Ar-H). GC-MS: 99.0%, m/z = 394.



Scheme S1. Synthetic route for synthesis of azo monomer.

Photoresponsive properties of the azo monomer film.

To study the photoresponsive properties of the azo monomer film, a solution of azo monomer in dichloromethane (10 mg·L^{-1}) was cast onto a quartz plate and form a thin film at room temperature. The as-synthesized azo monomer (3) is photoresponsive which corresponded to *trans*/*cis* isomerization of azobenzene groups under UV and visible light irradiation. With UV and visible light irradiation, reversible photoresponse was observed with azo monomer film. As shown in **Figure S1**, the initial as-synthesized azo monomer film exhibits the maximum absorption at about 328 nm, which is due to the π-π* transition bands of trans-azobenzene. After UV light irradiation, the intensity of the π-π* transition band at 328 nm decreases and a new peak of 446 nm appears due to the n-π* transition band. After visible light illumination, the spectrum of the azo monomer film recovers.

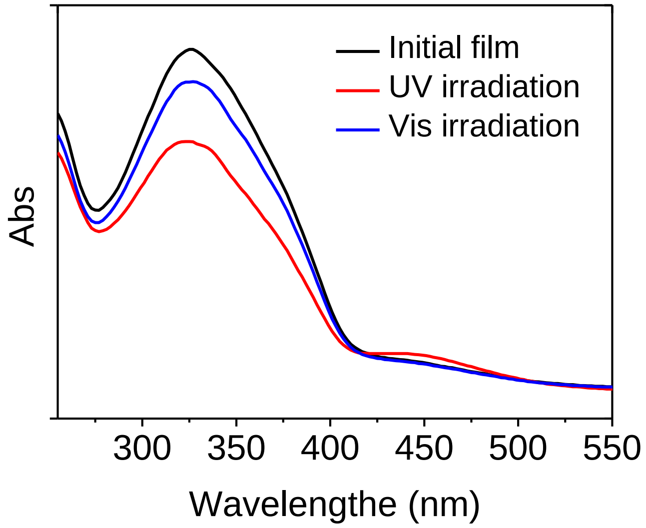


Figure S1. UV-vis spectra of azo monomer film with three sample states: as-synthesized, after UV-irradiation and after vis-irradiation.

S2. Synthesis of double-stimulus responsive wettability film with reverse pH responsibility

Synthesis of triblock copolymers PtBMA-b-PGMA-b-PMAAZO.

A solution of AIBN (0.0164 g, 0.1 mmol), CDB (0.136 g, 0.5 mmol), and *t*-BMA (2.8 g, 20 mmol) in benzene (3.0 mL) was degassed by three freeze-pump-thaw cycles, and then thermostated at 60°C under nitrogen atmosphere. After reaction for 12 h, GMA (1.4 g, 10 mmol) was added to the system by a syringe, and this reaction was allowed to proceed for another 2 h before quenched with liquid nitrogen. $M_{\mathrm{n,GPC}} = 4.5 \times 10^3$ g/mol and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.15$.

The resultant diblock copolymer was used as a polymeric chain transfer agent (macro-CTA) to initiate polymerization of azo monomer. A solution of azo monomer (1.0 g, 2.5 mmol), macro-CTA (0.18 g, 0.04 mmol), and AIBN (0.003 g, 0.02 mmol) in DMF (3.0 mL) was degassed by three freeze-pump-thaw cycles, and stirred at 70°C under nitrogen atmosphere for 48 h and then quenched with liquid nitrogen. $M_{\mathrm{n,GPC}} = 2.75 \times 10^4$ g/mol and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.23$.

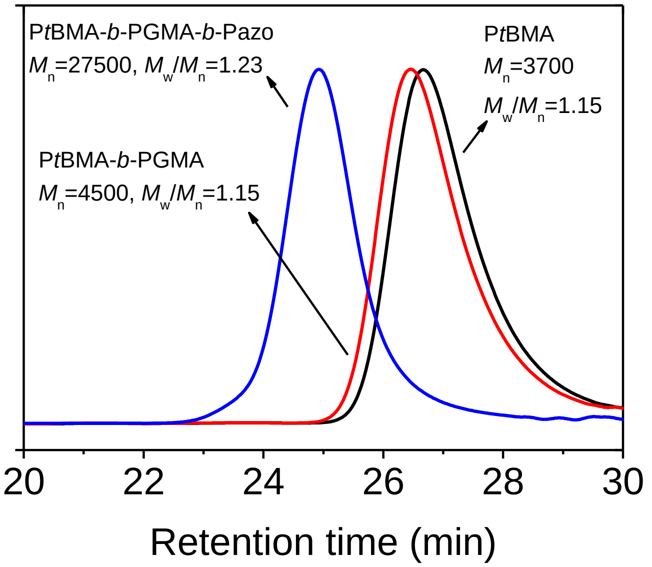


Figure S2. GPC monitoring the synthesis of copolymer PDPAEMA-*b*-PGMA-*b*-PMAAZO.

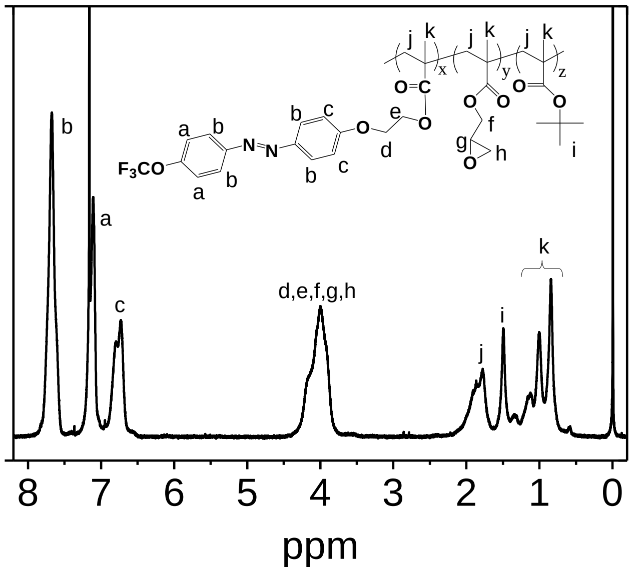


Figure S3. ^{1}H NMR spectra of triblock copolymer PDPAEMA-*b*-PGMA-*b*-PMAAZO.

Grafting of polymer Brushes onto amino-functionalized SiO_2 films.

SiO_2 films covered with V-shaped polymer brushes were prepared by grafting an ABC-type triblock copolymer, P*t*BMA-*b*-PGMA-*b*-PMAAZO, onto the surfaces of amino-functionalized SiO_2 films by employing a coupling reaction between epoxy and amine groups. The SiO_2 substrates were immersed into a DMF solution containing 2.5 wt% P*t*BMA-*b*-PGMA-*b*-PMAAZO and 0.5 wt% triethylamine at 70°C for 12 h. The substrates were washed with excess THF and dried in vacuum.

The polymer brush-grafted SiO_2 film substrates were then immersed into a dichloromethane solution containing 2 wt% TFA at room temperature for 24 h. Finally the substrates were washed with excess dichloromethane and dried in vacuum.

References

1. D. Prescher, T. Thiele, R. Ruhmann and G. Schulz, *J. Fuorine Chem.*, 1995, **74**, 185.