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## Supporting Information for

# Photo-responsive Superhydrophobic Surfaces for Effective Wetting Control

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#### **Movie Captions**

**Movie S1.** *Extreme water repellence of the artificial superhydrophobic surface.* Water drops (~5 mm in diameter) bounces off on the biomimetic surface freely without any residues.

**Movie S2.** *UV light induced wetting.* Water slowly wets the surface which has been illuminated with 365 nm UV light for 20 s, which results in final contact angle of  $\sim$ 43°.

**Movie S3.** *Visible light restored superhydrophobicity.* Ultra-low roll-off angle is restored via 90 s visible light irradiation at 425 nm, which corresponds to a contact angle of ~165°.

#### **Experimental Section**

**Materials.** Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 wt%), concentrated hydrochloric acid (HCl, 37 wt%), ammonia aqueous (NH<sub>3</sub>·H<sub>2</sub>O, 25 wt%), 6-chloro-1-hexanol (95 wt%), 4-(trifluoromethoxy)aniline, phenol, sodium hydroxide (NaOH), sodium nitrite (NaNO<sub>2</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), potassium hydroxide (KOH), potassium nitrate (KNO<sub>3</sub>), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), potassium iodide (KI), cetrimonium bromide (CTAB), tetraethyl orthosilicate (TEOS), iron(II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), toluene diisocyanate (TDI), dibutyltin dilaurate (DBTDL), tetrahydrofuran (THF), dimethyl formamide (DMF), toluene, ethanol, *n*-hexane, glycerol, and all solvents were purchased from Sinopharm. Toluene was freshly distilled in the presence of calciumhydride (CaH<sub>2</sub>) before each isocyanate-based "click reaction". Water was deionized and distilled before use. All other reagents were of analytical grade and used as received without further purification.

Synthesis of 4-((4-(trifluoromethoxy)phenyl)diazenyl)phenol (1). A total amount of 2.8 g 4-(trifluormethoxy)aniline was dissolved in 40 mL 2 M aqueous H<sub>2</sub>SO<sub>4</sub> and kept at 0 °C, followed by the dropwise addition of 16 mL 1 M sodium nitrite solution in water and stirred for 1 h. A total of 1.2 g sodium hydroxide, 15 g sodium carbonate and 1.6 g phenol were dissolved in 80 mL water and kept at 0 °C, followed by the dropwise addition of the former solution and stirred for 1 h. The resultant was then neutralized with 1 M aqueous HCl, filtered, washed with water and recrystallized from *n*-hexane. The melting point was measured to be 116.5~116.6 °C.

Synthesis of 6-(4-((4-(trifluoromethoxy)phenyl)diazenyl)phenoxy)hexan-1-ol (2). A total of 2.6 g compound 1, 1.6 g K<sub>2</sub>CO<sub>3</sub>, a trace amount of KI and CTAB were dissolved in 80 mL DMF, followed by dropwise addition of 10 mL 2.5 M 6-chloro-1-hexanol in DMF under string at 90 °C and kept for 24 h. The resultant precipitated from the solution by adding water. Orange yellow fluoro-AZO (compound 2) was finally obtained by filtration of the resultant and recrystallization from *n*-hexane. The melting point was measured to be 95.0~95.6 °C.

Synthesis of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles. A total of 0.7 g KOH and 5 g KNO<sub>3</sub> were dissolved in 150 mL water and purged with N<sub>2</sub> for 1 h, followed by addition of 80 mL 1 M FeSO<sub>4</sub>·7H<sub>2</sub>O solution under mechanical stirring and kept at 90 °C for 1 h. After cooling down to the room temperature, black Fe<sub>3</sub>O<sub>4</sub> nanoparticles of ~30 nm in diameter were collected and washed with ethanol six times, subsequently dried in the vacuum oven at room temperature.

Synthesis of  $Fe_3O_4@SiO_2$  Nanoparticles. A total of 200 mg  $Fe_3O_4$  nanoparticles were dispersed in the mixture of 80 mL ethanol, 20 mL water and 5 mL NH<sub>3</sub>·H<sub>2</sub>O under ultrasonication and mechanical stirring, followed by the dropwise addition of 200 µL TEOS within 20 mL ethanol. After stirred for 2 h, spherical  $Fe_3O_4@SiO_2$  nanoparticles of ~300 nm in diameter were finally collected and washed with ethanol and completely dried in vacuum oven at 35 °C for 24 h.

**Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NCO Nanoparticles.** A total of 100 mg Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were dispersed in 100 mL toluene by ultrasonication for 30 min, followed by dropwise addition of 200 mg TDI and 2 mg DBTDL within 10 mL toluene under N<sub>2</sub> atmosphere. The surface graft

reaction carried 60 °C under vigorous stirring was then out at for 3 h. Diisocyanate-functionalized magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NCO) were collected with the help of a magnet, washed with toluene for 6 times and dried in vacuum oven at 50 °C for 12 h.

**Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO Nanoparticles.** A total of 50 mg Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NCO nanoparticles were redispersed in 100 mL toluene by mechanical stirring under N<sub>2</sub> atmosphere, followed by the dropwise addition of 50 mg fluoro-AZO and a trace amount of DBTDL within 10 mL toluene. The mixture was then refluxed at 80 °C for 4 h. Fluoro-AZO functionalized magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO) were separated by a magnet, washed with toluene and ethanol for three times respectively and dried in vacuum oven at 35 °C for 12 h.

**Fabrication of Biomimetic Superhydrophobic Coatings.** Hydrophobic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO nanoparticles were used for the fabrication of ultra-low contact angle hysteresis biomimetic superhydrophobic surfaces. 10 mL suspension of 20 mg/ml nanoparticles with 1 wt% fluoro-AZO in ethanol was sprayed directly onto a piece of silicon wafer ( $2 \times 4$  cm) using an air brush (Paasche Airbrush Co.) at a distance of 20 cm with an N<sub>2</sub> pressure of 50 psi. The substrate was subsequently dried in the vacuum oven at room temperature for 1 h.

**Surface Wetting Control.** The surface wetting behaviors of the biomimetic superhydrophobic coating could be accurately adjusted by controlling the molecular configurations (*Trans* and *Cis* states) of fluoro-AZO units. A Xe lamp (Trusttech CHF-XM-500W) equipped with a cut filter for UV (365 nm) and visible light (425 nm) irradiation was used to alternate the *Trans* and *Cis* 

states of fluoro-AZO units. The surface wettability, characterized by water contact angles, was finely controlled by UV or visible light illumination with different exposure time (0~90 seconds). The demonstration of surface switchable wettability was conducted by UV irradiation for 30 seconds (*i.e.* superhydrophilic) and visible light illumination for 90 seconds (*i.e.* superhydrophobic) alternately.

**Surface Free Energy Estimation.** Flat glass slide was first cleaned with ethanol and acetone respectively and then spin-coated with 20 mg/ml solution of fluoro-AZO in THF at 1500 RPM for 30 seconds. The surface was subsequently dried in the vacuum oven at room temperature. Contact angles of probe liquids (water and glycerol) on the coating were obtained after 30 seconds UV and/or 90 seconds visible light illumination. Owens-Wendt<sup>1</sup> approach was used to estimate the solid surface free energy of fluoro-AZO coating.

Water Flow Control. A piece of filter paper was first dip-coated with the suspension of spherical magnetic nanoparticles in ethanol with a solid content of 50 mg/mL. After drying, the coated filter paper was tightly sandwiched between two glass tubes (with an inner diameter of 1 cm). 3 mL of red ink was poured into the setup and blocked above the filter paper owing to the superhydrophobicity of coated nanoparticles. Red ink passed through the filter paper after irradiated by UV light for 30 seconds. The water resistance of the coated filter paper would be restored by applying visible light illumination for 90 seconds.

Characterization. The surface morphologies of superhydrophobic coatings were observed by field-emission scanning electron microscope (SEM, JSM 6700F) at an accelerating voltage of 10 kV. The core-shell structures of magnetic nanoparticles were characterized by transmission electron microscope (TEM, JEM 3010) at an acceleration voltage of 100 kV. The microscopic contours of the rough surface and the flat spin-coating were measured with atom force microscope (AFM, Seiko SPA400) by tapping mode. The encapsulation of magnetic nanoparticles was confirmed by energy dispersive X-ray spectrum (EDX, JSM 6700F) with an accelerating voltage of 5 kV. The surface chemical composition of nanoparticles was measured by Fourier transform infrared spectra (FT-IR, Nexus 670) between 4000 and 400 cm<sup>-1</sup> in the form of KBr pellets. The chemical structures of fluoro-AZO molecules were confirmed by proton nuclear magnetic resonance spectrometer (<sup>1</sup>H NMR, Bruker 300MHz) with CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. The thermal stability of the nanoparticles (ca. 7 mg) was investigated with thermogravimetric analysis (TGA, Henven HCT-1) under nitrogen or air atmosphere from room temperature (ca. 30 °C) to 800 °C at a heating rate of 10 °C/min. The photoisomerization of fluoro-AZO units was confirmed by ultraviolet-visible absorption spectrophotometer (UV-Vis, Vary 300) with a scan range of 350~650 nm using THF as the solvent or dispersant. Magnetization curves of nanoparticles were obtained at room temperature (300 K) with a susceptometer (MPMS-5 DC SQUID). The contact angle (CA) measurements were conducted with a goniometer (DSA100 KRUSS) using a small volume of liquid (ca. 5 µL). The sliding angles (SA) were measured by tilting the stage until a droplet (ca. 5 µL) rolled off from the surface. At least five measurements were performed to

obtain each value. The error in contact angle and roll-off angle was averaged within  $\pm 2^{\circ}$  and  $\pm 0.5^{\circ}$ , respectively. The surface resistance to water or ink was also recorded using a digital camera (Olympus E-P3).



Figure S1. Synthesis of target photo-responsive fluoro-AZO derivative.



Figure S2. <sup>1</sup>H NMR spectrum of 4-((4-(trifluoromethoxy)phenyl)diazenyl)phenol (1).



Figure S3. <sup>1</sup>H NMR of 6-(4-((4-(trifluoromethoxy)phenyl)diazenyl)phenoxy)hexan-1-ol (2).



**Figure S4.** Schematic chemical compositions of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO nanoparticles. As to anchor fluoro-AZO onto the magnetic nanoparticle surface, toluene diisocyanate (TDI) first reacted with the abundant silanol at the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> to obtain Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NCO nanoparticles covered by reactive isocyano-groups (-NCO) at the surface, which could further react with fluoro-AZO to obtain the final Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO nanoparticles.



**Figure S5.** EDX spectrum of the core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles. Only absorption peaks of Si and O were observed revealing the magnetic nanoparticles were fully encapsulated by SiO<sub>2</sub> during the sol-gel process of Stöber method.



Figure S6. FT-IR spectra (left) and TG curves (right) of the as-prepared nanoparticles. As is indicated in the FT-IR spectra, the virtually elimination of the strong absorption peak at 2278 cm<sup>-1</sup> ascribed to the isocyano group at the nanoparticle surface (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NCO), implying the successful grafting of fluoro-AZO onto the magnetic nanoparticle surface (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO). The thermogravimetric curves of the nanoparticles were obtained under nitrogen at a heating rate of 10 °C min<sup>-1</sup>. The magnetic nanoparticles are thermal stable in N<sub>2</sub> atmosphere from room temperature up to  $T \approx 280$  °C. Based on the weight losses at T = 750 °C revealed from the TG curves, the -NCO density of the TDI modified magnetic hybrid is calculated to be 0.71 mmol g<sup>-1</sup>, a high content that provides convenient platform for the further functionalization. The final fluoro-AZO content is calculated to be 0.16 mmol g<sup>-1</sup>, implicating a reasonable graft yield of 22.5% (mol/mol) respect to the -NCO content, which is mainly attributed to the hydrolysis of -NCO and stereo-hindrance effect of the relatively large fluoro-AZO molecules.



**Figure S7.** Standard paramagnetic characteristic curves with no hysteresis (top) and response to external magnetic field (bottom). The magnetization properties of the as prepared nanoparticles were investigated with a susceptometer at 300 K. The saturated magnetization of pure Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO was found to be 60 emu g<sup>-1</sup> and 45 emu g<sup>-1</sup> at 300 K, respectively. The reduction of the magnetization value for the surface functionalized nanoparticles can be attributed to the thin SiO<sub>2</sub> layer. The fluoro-AZO functionalized magnetic nanoparticles response quickly to the external magnetic field. Well dispersed nanoparticles in ethanol can be quickly separated within few seconds from the suspension with very high efficiency, the property of which is quite useful in the separation of dyes and drugs from industrial wastewater. Time interval is ~ 2 s. Scale bar is 10 mm.



Figure S8. TG curves of pure Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO nanoparticles in air. Owing to the water absorption, oxidation of carbon and Fe<sub>3</sub>O<sub>4</sub>, an upward swing of the TG curves can be observed prior to the bulk of the weight loss. Substantial weight loss of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO at  $T \approx 750$  °C indicates fluoro-AZO was successfully grafted onto the surface. The total weight of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO nanoparticles attains to the maximum value of 14.8 wt% at  $T \approx 100$  °C (close to the melting point  $T_m = 95^{\circ}$  C of fluoro-AZO), and starts to slowly dehumidify around  $T \approx 150$  °C with a striking decrease starting approximately at  $T \approx 250$  °C, finally retains with a total weight of 80 wt% at  $T \approx 750$  °C. The outstanding upward swing at low temperatures accounts for a net weight gain of 11.6 wt% for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO nanoparticles respect to pure Fe<sub>3</sub>O<sub>4</sub> (3.2 wt% weight gain), which may be mainly attributed to the water absorption caused by conformation change of azobenzene units (transforming from Trans state to Cis state upon heating), thus turning the hydrophobic fluoro-AZO ( $\theta_{e,trans} = 105^{\circ}$ ) into hydrophilic ( $\theta_{e,cis} = 23^{\circ}$ ) and forming strong hydrogen bonds with water in air. The calculated water absorption capacity is 8.17 mmol g<sup>-1</sup> by assuming that the oxidation of carbon and Fe<sub>3</sub>O<sub>4</sub> at low temperatures is negligible thus not accounting for the weight gain.



**Figure S9.** Stain removal on the hydrophobic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO nanoparticles. Black ink drop on the as-prepared hydrophobic powder can be easily and completely removed without any stain residue. Scale bar is 2 mm.



Figure S10. Switchable surface wettability and surface free energy.



**Figure S11.** AFM images of the spin-coated fluoro-AZO. The phase separation of fluoro-AZO renders the nanoscale roughness which promotes the surface wetting and/or de-wetting upon light illumination. Scale bar is 200 nm.



Figure S12. Molecule length of fluoro-AZO of extended or *Trans* configuration under visible light (left) and bent or *Cis* configuration under UV light (right), which is shorter by  $\sim$ 7 Å.



**Figure S13.** UV-Vis absorption spectra of fluoro-AZO molecule and the modified Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-AZO nanoparticles. The spectra change considerably as a result of *Trans-Cis* conversion. The maximum absorption of the Fluoro-AZO azobenzene solution appears around 347 nm with a weak band near 435 nm, owing to the  $\pi$ - $\pi$ \* and n- $\pi$ \* transition bands of *Trans* state, respectively. Upon UV irradiation, the  $\pi$ - $\pi$ \* transition is deterred but the n- $\pi$ \* transition is promoted owing to the *Cis* state of fluoro-AZO molecule. Upon visible light illumination, the spectrum of the azobenzene solution recovers. The fluoro-AZO modified magnetic nanoparticles exhibit similar absorption characteristics but much lower density compared with that of fluoro-AZO molecules, which could be attributed to the dissipation of the nanoparticle solution.



Figure S14. SEM image of coated filter paper displaying controlled wettability.

#### **Supplementary Discussions**



#### Section S1. Contact Angle Estimation

**Figure S15.** Schematic diagram of the cross section of spherical surfaces and characteristic geometrical parameters used in Wenzel and Cassie-Baxter relations.

To theoretically quantify the surface performance about wetting, parameters are defined above according to the literature<sup>2</sup>.  $\phi_s$  is the area fraction of the air-liquid interface occluded by the surface texture (*i.e.* the ratio of the projected wet area to the total projected area).  $r_{\phi}$  is the surface roughness of the wetted region (*i.e.* the ratio of the actual contacting surface to the projected wetted area). r is the global surface roughness (*i.e.* the ratio of the total surface area to the projected area). Thus, for a partially wetted surface ( $\theta_e > 0^\circ$ ) shown above, the area fraction of liquid-solid interface is  $f_{sl} = r_{\phi}\phi_s$  and that of liquid-air interface is  $f_{lv} = 1 - \phi_s$ .



**Figure S16.** Schematic diagram shows a water drop resides on the substrate (left) in Wenzel state and the zoom-in interface (right) illustrating the local water-solid contact.

A fully wetted Wenzel interface takes the consideration that water locally fully wet the surface  $(\theta_{local} \equiv 0^\circ \neq \theta_e)$  and no air is trapped under the water drop  $(\phi_s \equiv 1)$ , thus the apparent water contact angle  $\theta^*$  is the function of surface roughness<sup>3</sup>:

$$\cos\theta^* = r\cos\theta_e \qquad (S1)$$

As for a fully wetted surface composed of *hexagonal or equilateral triangular arrangement of discrete spheres*, we have:

$$r = \frac{S_{sphere} + S_{project}}{S_{project}} = \frac{2\pi R^2}{\frac{1}{2}(2R + 2D)\frac{\sqrt{3}}{2}(2R + 2D)} + 1 = \frac{2\pi}{\sqrt{3}D^*} + 1$$
(S2)

Thus, Equation S1 becomes:

$$\cos\theta^* = \left(\frac{2\pi}{\sqrt{3}D^*} + 1\right)\cos\theta_e \qquad (S3)$$

Note that, the coefficient in Equation S3 representing the surface roughness may be much greater than unit (which is consistent with the original Wenzel model). Up to a point the value of calculated  $\cos\theta^*$  will reach the maximum "1" – predicting a fully wetted state (i.e.  $\theta^* = 0$ ), and beyond the point the surface will maintain superwetting sate and thus is independent with the surface roughness (*i.e.* false value of  $\theta^*$ ). In other words, if the case of calculated  $\cos\theta^* \ge 1$  is reached the surface is considered to be fully wetted by water by maintain a zero contact angle.



**Figure S17.** Schematic diagram shows a water drop ball-up the substrate (left) in composite Cassie-Baxter state and the zoom-in interface (right) illustrating the local air-water-solid contact.

For a partially wetted surface, system free energy will reach global minimum as the apparent contact angle  $\theta^*$  of the composite interface attains a value derived from the following Cassie-Baxter relations<sup>4-7</sup>:

$$\cos\theta^* = f_{sl}\cos\theta_e - f_{lv} \qquad (S4)$$

$$\cos\theta^* = r_{\phi}\phi_s\cos\theta_e + (1-\phi_s)\cos\theta_a \qquad (S5)$$

As for a partially wetted surface featured by *hexagonal or equilateral triangular arrangement* of discrete spheres, we have<sup>8</sup>:

$$r_{\phi} = \frac{\pi R^2 \left(1 + \cos \theta_e\right)}{\frac{1}{2} \pi \left(R \sin \theta_e\right)^2} = \frac{2\left(1 + \cos \theta_e\right)}{\sin^2 \theta_e}$$
(S6)

$$\phi_s = \frac{\frac{1}{2}\pi (R\sin\theta_e)^2}{\frac{1}{2}(2R+2D)\frac{\sqrt{3}}{2}(2R+2D)} = \frac{\pi\sin^2\theta_e}{2\sqrt{3}D^*}$$
(S7)

Thus, Cassie-Baxter relation and the interface fractions can be transformed as:

$$\cos\theta^* = -1 + \frac{1}{D^*} \left[ \frac{\pi}{2\sqrt{3}} (1 + \cos\theta_e)^2 \right]$$
 (S8)

$$f_{sl} = \frac{\pi (1 + \cos \theta_e)}{\sqrt{3}D^*} \qquad (S9)$$

$$f_{lv} = 1 - \frac{\pi \sin^2 \theta_e}{2\sqrt{3}D^*} \qquad (S10)$$

## Table S1. Summary of equations for contact angle estimation.

Model	Wenzel Regime	Cassie-Baxter Regime	
Schematic diagram	Water Substrate	Water Air Substrate	
Hexagonally arranged sphere	$\cos\theta^* = \left(\frac{2\pi}{\sqrt{3}D^*} + 1\right)\cos\theta_e$ $r_{\phi} = \frac{2\pi}{\sqrt{2}\pi} + 1$	$\cos\theta^* = -1 + \frac{1}{D^*} \left[ \frac{\pi}{2\sqrt{3}} (1 + \cos\theta_e)^2 \right]$ $r_{\phi} = \frac{2(1 + \cos\theta_e)}{\sin^2\theta}$	
array	$\sqrt[4]{} \sqrt{3D^*}$ $\phi_s = 1$	$\phi_s = \frac{\pi \sin^2 \theta_e}{2\sqrt{3}D^*}$	

Working Surfaces	Adv. CA	Rec. CA	Static CA	Sliding Angle
Spin-coating of Fluoro-AZO	110	95	105	23
Sprayed spherical particle coating (Visible light)	166	165	165	0.5
Sprayed spherical particle coating (UV light)	5	0	0	_
Sprayed filter paper (Visible light)	157	153	155	1.0
Sprayed filter paper (UV light)	8	0	0	_

Table S2. Surface property subject to light exposure

Note: Unit of above items is degree (°). Derivation for contact angle is  $\pm 2^{\circ}$  and sliding angle  $\pm 0.5^{\circ}$ .  $\sim 5 \ \mu L$  water droplet applied.

#### Section S2. Surface Energy Estimation

Probe Liquid	Surface Tension (mN/m)		Contact Angle $\theta_e$ (deg)		
	Dispersive $\gamma_{lv}^d$	Polar $\gamma_{lv}^d$	Total $\gamma_{lv}$	Trans State	Cis State
Water	21.8	51.0	72.8	105	23
Glycerol	34.0	30.0	64.0	93	13

**Table S3.** Liquid surface tension and contact angle on the spin-coated surface.

Note: Derivation for contact angle is averaged within  $\pm 2^{\circ}$ .

Flat glass slide was first cleaned with ethanol and acetone respectively and then spin-coated with 20 mg/ml solution of fluoro-AZO in THF at 1500 RPM for 30 seconds (Figure S11). The surface was subsequently dried in the vacuum oven at room temperature. Contact angles of probe liquids (water and glycerol) on the coating were obtained after 30 seconds UV and/or 90 seconds visible light illumination. Owens-Wendt approach<sup>1</sup> was used to estimate the solid surface free energy of fluoro-AZO coating.

$$\frac{1}{2} \left( 1 + \cos \theta_e \right) \gamma_{lv} = 2 \sqrt{\gamma_{sv}^d \gamma_{lv}^d} + 2 \sqrt{\gamma_{sv}^p \gamma_{lv}^p} \qquad (S11)$$

Here surface free energy of liquid  $(\gamma_{lv})$  or solid  $(\gamma_{sv})$  could be written  $\gamma_{lv} = \gamma_{lv}^d + \gamma_{lv}^p$  and  $\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p$ , respectively, where the superscripts *p* and *d* refer to the dipole-hydrogen bonding and dispersion force components. Surface tension components and contact angles of the probe liquids on the spin-coated surface are listed above.

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