Supplemental Information

Light-Driven Macroscopic Directional Motion of Water Droplet on an Azobenzene–Calix[4]arene Modified Surface

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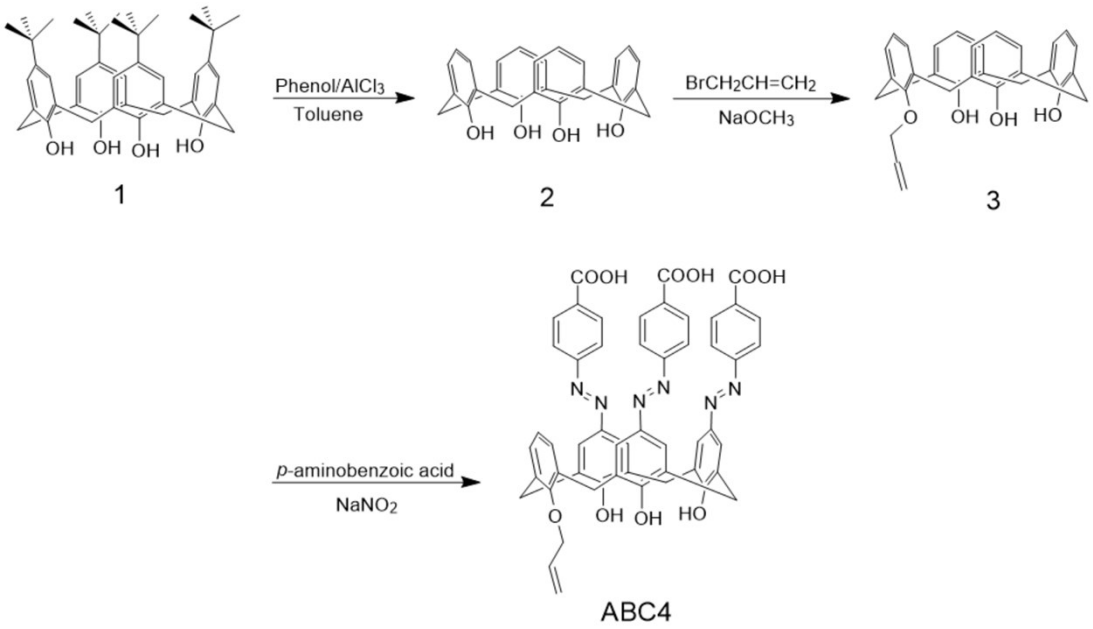
Contents

1. The synthesis of azobenzene-calix[4]arene (ABC4)



Scheme S1. The synthesis route of azobenzene-calix[4]arene (ABC4).

1.1 Synthesis of compound 3[S1]

Sodium methoxide (0.39 g) and compound 2 (2.00 g) in acetonitrile (100 mL) was stirred at reflux for 0.5 h. Allyl bromide (0.6 mL) was added and the reaction mixture was stirred at reflux for a further 8 h. The solvent was evaporated and the residue was dissolved in trichloromethane (30 mL). The organic solution was washed diluted HCl and water then dried with sodium sulphate. Evaporation of the solvent gave a crude solid. The crude product was purified by column chromatography (petroleum ether/ trichloromethane (v/v)=4/1) to yield the desired compound 3 (1.49 g, yield 68%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.58 (s, 1H, ArOH), 8.90 (s, 2H, ArOH), 7.30-6.96 (m, 8H, ArH), 6.85 (s, 1H, ArH), 6.62 (s, 3H, ArH), 6.35 (m, 1H, CH=CH$_2$), 5.74 (d, J = 16.4 Hz, 1H, CH=CH$_2$), 5.49 (d, J = 10.7 Hz, 1H, CH=CH$_2$), 4.63 (s, 2H, OCH$_2$), 4.33-4.13 (t, 4H, ArCH$_2$Ar), 3.47 (dd, J = 23.8, 13.2 Hz, 4H, ArCH$_2$Ar) ppm.

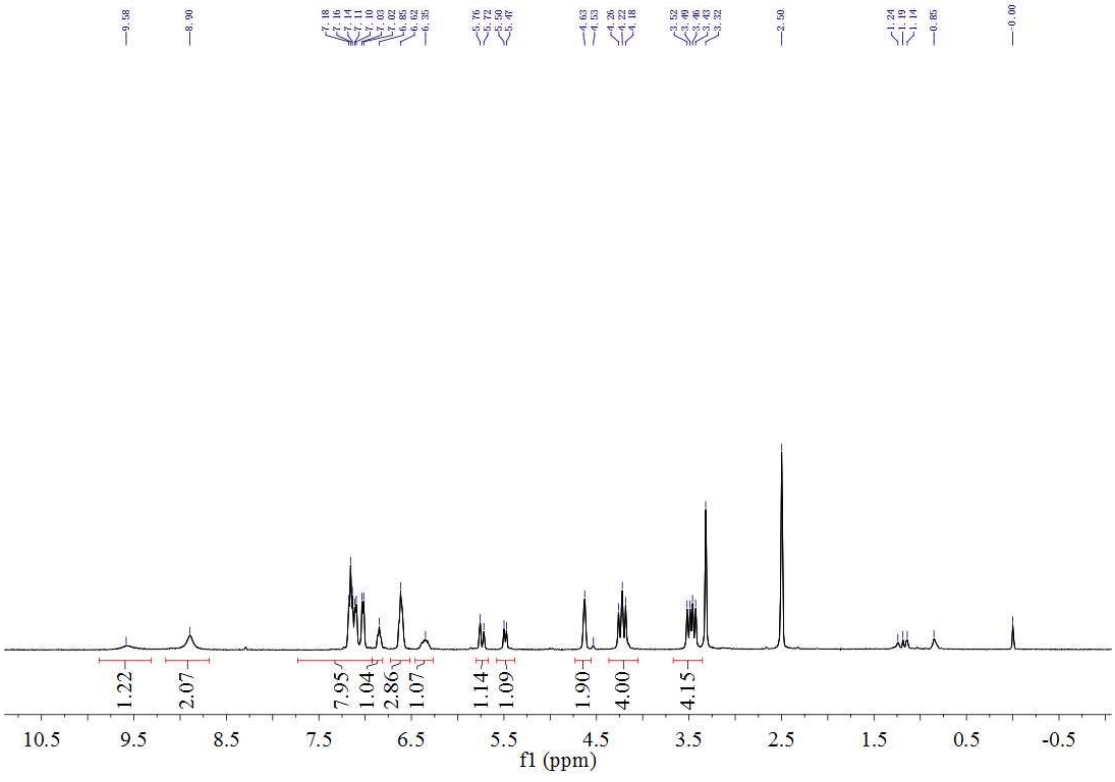


Figure S1. ^{1}H NMR (400M Hz, DMSO-d_6, 25℃) of compound 3.

1.2 Synthesis of ABC4[S2]

p-aminobenzoic acid (0.93 g) and hydrochloric acid (1.5 mL) in water (15 mL) was stirred about 2 min. Then this solvent was cooled to -10℃. The $NaNO_2$ (0.49 g) aqueous solution (6mL) was added to *p*-aminobenzoic acid solvent drop by drop. After the dropwise addition, the solvent was pale-yellow and clarified liquid (1).

Compound 3 (0.7 g) and anhydrous sodium acetate (1.6 g) was dissolved in DMF (16 mL) and methanol (10 mL). the solvent was cooled to -5℃. And then, liquid (1) was added in this solvent drop by drop. After the dropwise addition, the reaction system was stirred about 6 h at -5℃. To Stop the reaction, diluted HCl (50 ml, 0.1M) was added in it and continued to react about 2 h. After filtration, the solid was washed with water (30 mL) and methanol (30 mL) to give a crude solid. Lastly, the crude solid was purified by recrystallization to obtain the ABC4 (1.20 g, yield 88%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 14.66-11.38 (s, 2H, COOH), 10.58-8.99 (s, 2H, COOH), 8.13 (d, *J* = 7.4 Hz, 4H, ArH), 8.07-7.96 (m, 4H, ArH), 7.90 (dd, *J* = 21.8, 13.3 Hz, 6H, ArH), 7.82-7.51 (m, 4H, ArH), 7.15 (d, *J* = 7.2 Hz, 2H, ArH), 6.84 (d, *J* = 7.0 Hz, 1H, ArH), 6.29 (m, 1H, $CH{=}CH_2$), 5.74 (d, *J* = 16.6 Hz, 1H, $CH{=}CH_2$), 5.44 (d, *J* = 10.2 Hz, 1H, $CH{=}CH_2$), 4.61 (s, 2H, OCH_2), 4.39 (dd, *J* = 48.7, 12.7 Hz, 4H, $ArCH_2Ar$), 3.77 (dd, *J* = 37.8, 12.7 Hz, 4H, $ArCH_2Ar$) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 206.30, 166.74, 154.45, 152.56, 151.50, 145.10, 133.62, 133.36, 133.10, 132.90, 131.58, 130.51, 129.13, 128.84, 128.48, 127.61, 125.28, 124.94, 124.63, 123.8, 121.83, 119.03, 117.61, 76.70, 76.48, 35.70, 30.73, 30.59 ppm. ESI(+)MS calcd for $C_{52}H_{40}N_6O_{10}$ 908.28 (M^+), found: m\z =931.508 ($M+Na^+$).

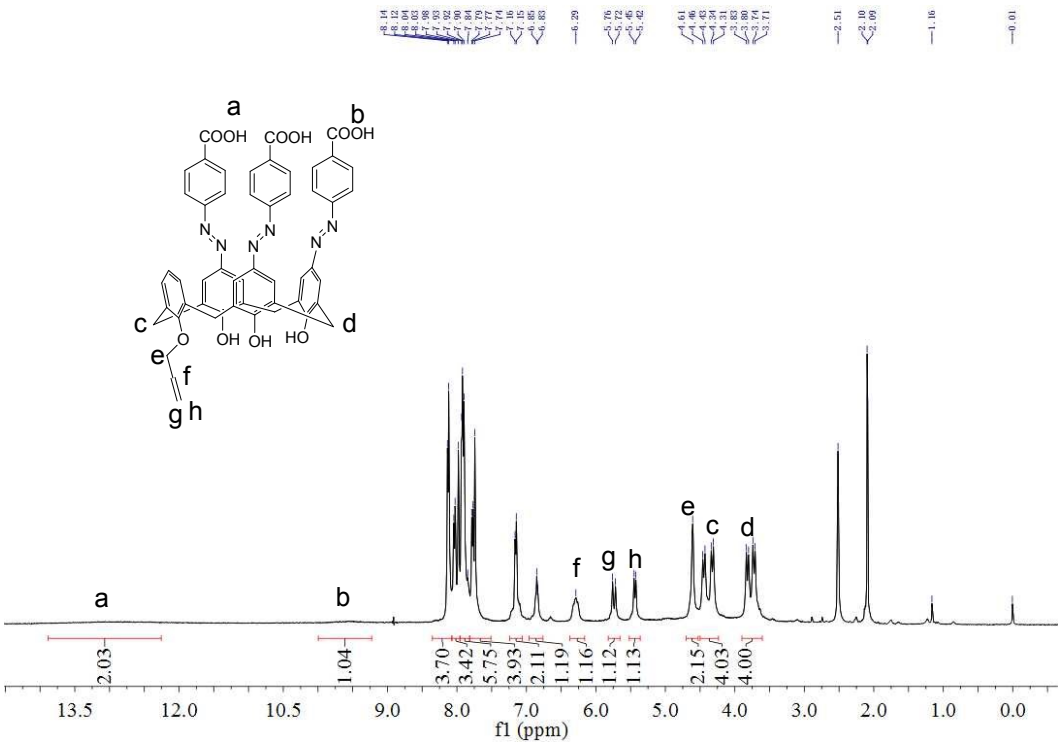


Figure S2. ^{1}H NMR (400M Hz, DMSO-d_6, 25℃) of ABC4.

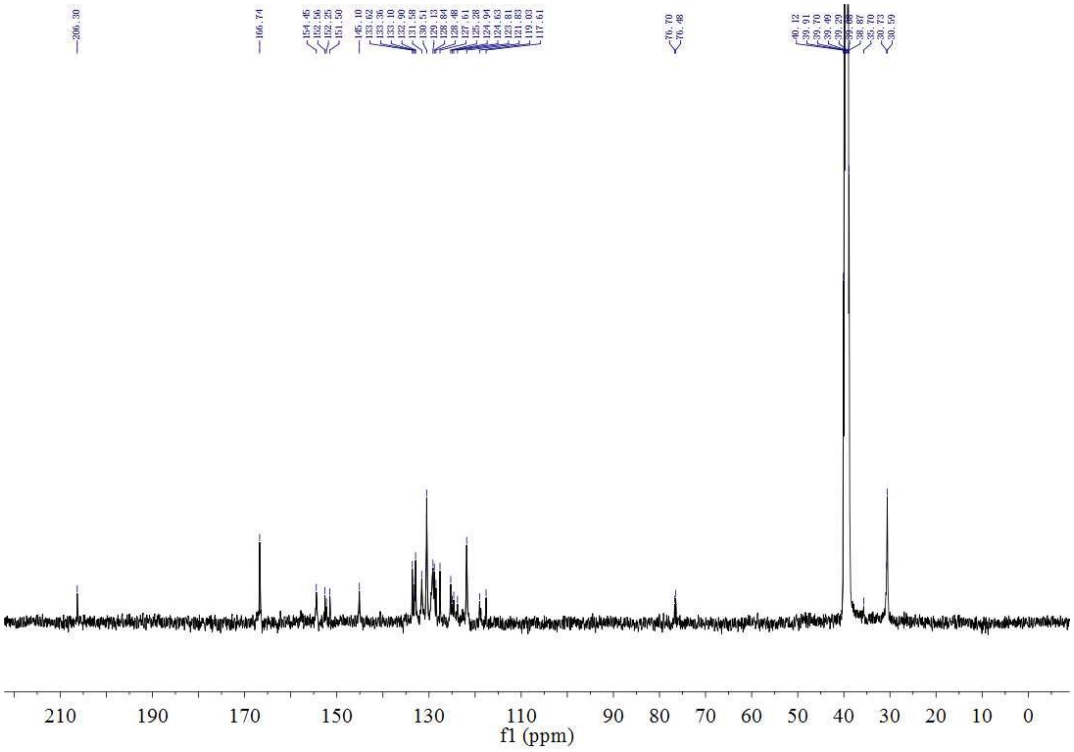


Figure S3. ^{13}C NMR (100M Hz, DMSO-d_6, 25℃) of ABC4.

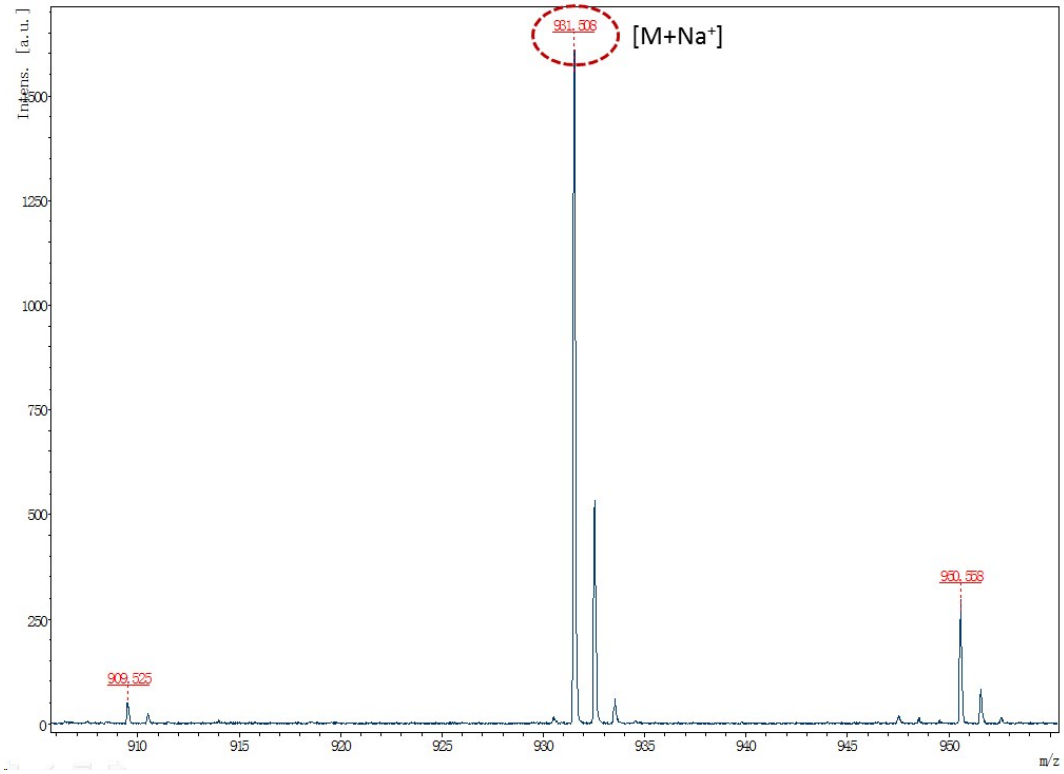


Figure S4. Mass spectrum of ABC4.

2. Responsive time of ABC4 to UV light

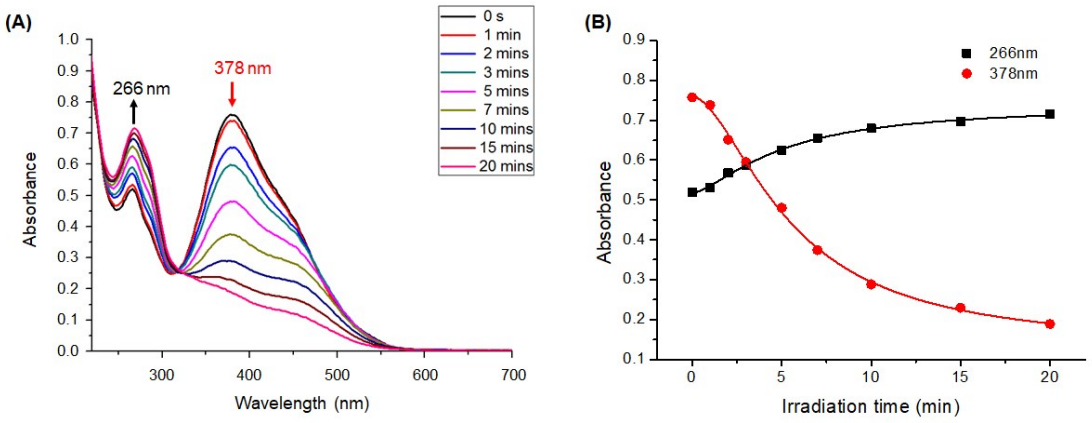


Figure S5. (A) The UV-Vis spectra of 1×10^{-5} M *trans*-ABC4 after irradiation at 365 nm for different time; (B) The changes of absorbance at 266 nm and 378 nm with irradiation time. The absorption band at 378 nm decreased gradually as the irradiation went on.

3. Photoisomerization of ABC4 on ^{1}H NMR spectrum

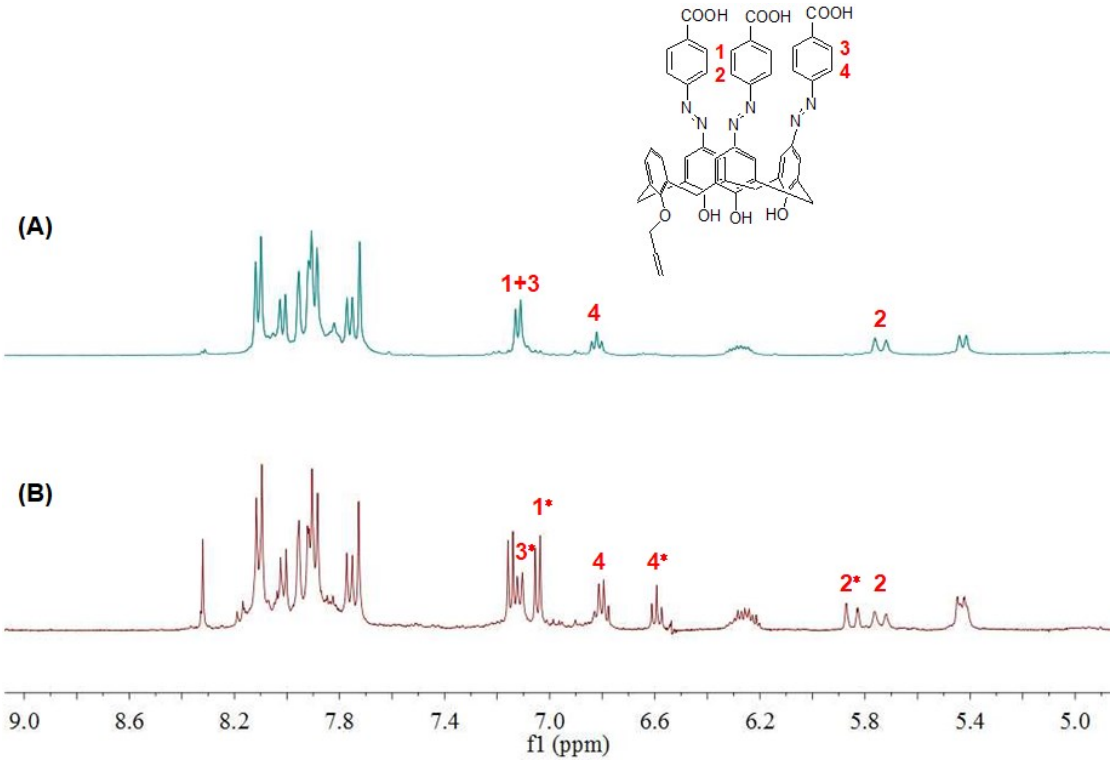


Figure S6. The partial ^{1}H NMR spectra of (A) 1 mM *trans*-ABC4 and (B) 1 mM *trans*-ABC4 after irradiation at 365 nm for 20 min, the four new signals (Protons H1*, H2*, H3* and H4*) indicated *trans*-to-*cis* isomerization occurred among ABC4.

4. Gaussian calculation and three-dimensional coordinates of ABC4

The optimized structures were obtained by computational calculations at HF/6-31g(d) levels by using Gaussian 09.

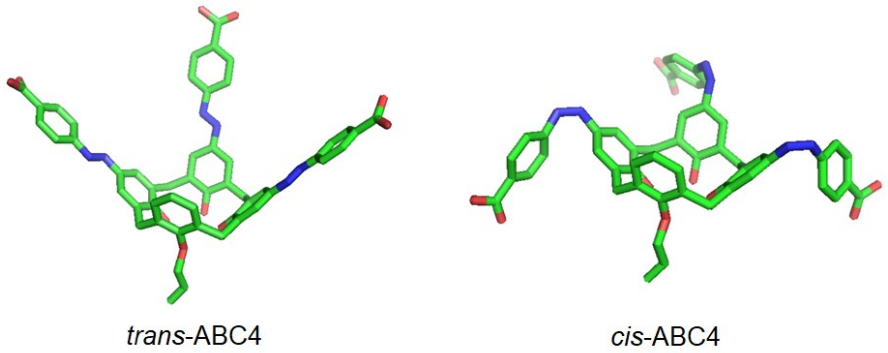


Figure S7. Energy-minimized structures of *trans*-ABC4 and *cis*-ABC4, optimized at the HF/6–31G(d) level.

Table S1. Energy difference between *trans*-ABC4 and *cis*-ABC4.

	Energy (a.u.)	**ΔEnergy (a.u.)**	**ΔEnergy (kcal/mol)**
trans-AZC4	-3067.67464479		
cis-AZC4	-3067.58930549		
E_{cis} - E_{trans}		0.0853393	53.55

Computational structure of *trans*-ABC4

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Cartesian Coordinates (XYZ format)

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Computational structure of *cis*-ABC4

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cis-Azo-C4

0 1

Cartesian Coordinates (XYZ format)

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H	-6.86065400	-3.44231000	-0.47063200
H	-8.19750300	-2.88313700	1.52290200
H	-8.07747600	0.20642300	-2.30039200

5. Modification of ABC4 and contact angle (CA) tests

The etched silicon substrate was immersed in the chromic acid solution for about 2 h, washed three times with distilled water, and then dried under N_2 flow. After that, the silicon substrate was soaked in HF aqueous solution (v/v=25/1) for 10 min, then washed with distilled water and dried dry under N_2 flow to obtain the Si-H modified surface.

The ABC4 was attached onto surface by hydrosilylation addition reaction. The Si-H modified silicon substrate was reacted with ABC4 (8 mg) in THF (10 mL) at 30℃ under N_2 atmosphere, using $H_2PtCl_6 \cdot 6H_2O$ as a catalyst, to afford ABC4-modified silicon surface.

Contact angles (CA) were measured using an OCA 20 contact angle system (Dataphysics, Germany) at ambient temperature and saturated humidity. Before the contact angle test, the sample was blown dry with N_2 flow. In each measurement, an about 2 μL droplet of water was dispensed onto the surface of silicon substrate. The average contact angle value was obtained at five different positions of the same sample.

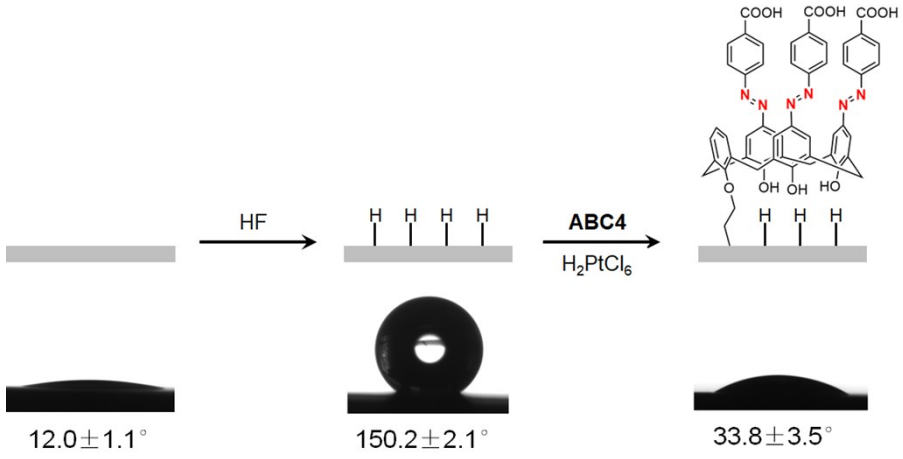

Figure S8. The modification process of ABC4 and contact angle characterization.

6. XPS characterization

X-ray photoelectron spectra (XPS) data were obtained with an ESCA-Lab220i–XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. All peaks were referenced to C1s (CHx) at 284.6 eV in the deconvoluted high-resolution C1s spectra. The analysis software was used as provided by the instrument's manufacturer.

Table S2. The XPS data of ABC4 modified silicon surface.

Name	Start BE	Peak BE	End BE	Height Counts	FWHM eV	Area (P) CPS.eV	Area (N)	At. %
C1s	291.04	284.6	281.8	26945.66	2.2	72835.89	28671.1	59.2
N1s	405.55	400.09	397.15	2555.67	2.31	6759.13	1493.15	3.08
O1s	535.9	532	529.15	56137.34	2.12	132864.13	18266.2	37.72

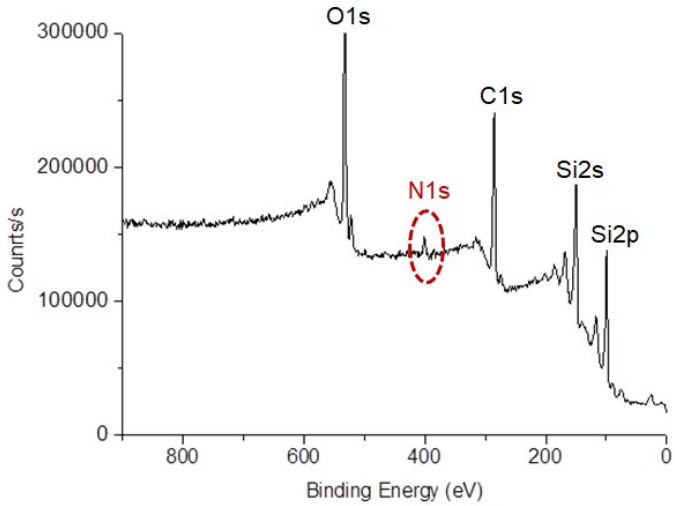

Figure S9. The XPS spectrum of the ABC4-modified silicon substrate, which indicates that the ABC4-SAMs were successfully constructed.

7. Photo-reversibility of ABC4-SAMs

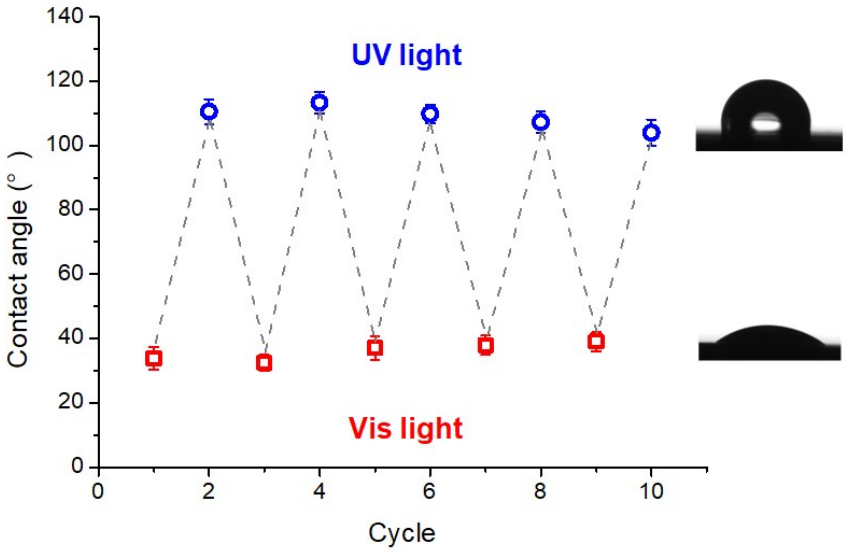

Figure S10. The photo-controlled cycling experiment on contact angle of ABC4-SAMs, the irradiation time for UV light and Vis light are 10 min and 30 min, respectively. The result illustrated good photo-recyclability of ABC4-SAMs.

8. Calculation of surface free energy ($\gamma_{s\text{-}g}$)[S3]

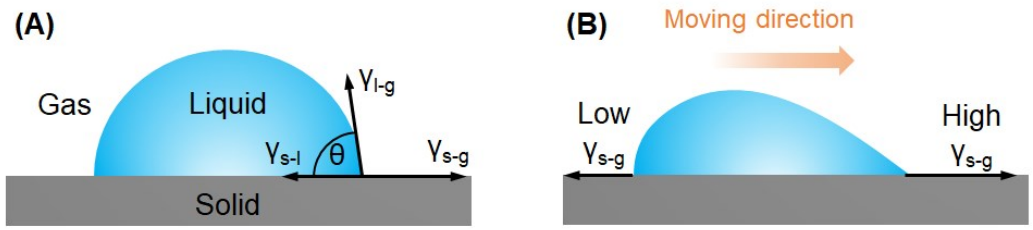

Figure S11. (A) Young model[S4]; (B) Droplet movement on free energy gradient surface[S5].

The basic theory of the liquid contact angle on a flat surface can be described by Young's equation (Formula 1) proposed by Young in 1805, which describes the relationship between the static contact angle (θ) of a droplet and the surface free energy of three interfaces (solid–liquid, solid–gas, and gas–liquid) (Figure S11):

$$\gamma_{s-g} = \gamma_{s-l} + \gamma_{l-g} \cdot \cos\theta \qquad \text{Formula (1)}$$

$$\gamma_{s-l} = \gamma_{s-g} + \gamma_{l-g} - 2\sqrt{\gamma_{s-g} \cdot \gamma_{l-g}} \qquad \text{Formula (2)}$$

where $\gamma_{s\text{-}g}$, $\gamma_{s\text{-}l}$ and $\gamma_{l\text{-}g}$ are the surface free energy of the solid-gas interface, the solid-liquid interface and the liquid-gas interface, respectively. And θ is the contact angle between the solid and the measuring liquid.

$$\gamma_{s-g} = \frac{(1+\cos\theta)^2}{4} \cdot \gamma_{l-g} \qquad \text{Formula (3)}$$

Formula (3) is obtained from Formula (1) and Formula (2) to calculate the surface free energy ($\gamma_{s\text{-}g}$) of solid–gas surface. For water, the $\gamma_{l\text{-}g}$ is 72.8 mN/M at 25℃.

Table S3. The calculation of surface free energy ($\gamma_{s\text{-}g}$).

	Water contact angle θ (°)	Surface free energy $\gamma_{s\text{-}g}$ (mJ/m^2)
trans-ABC4-SAMs	33.8±3.5°	61.0±2.2
cis-ABC4-SAMs	110.5±3.9°	7.7±1.5

9. Dynamic contact angle of water droplet movement

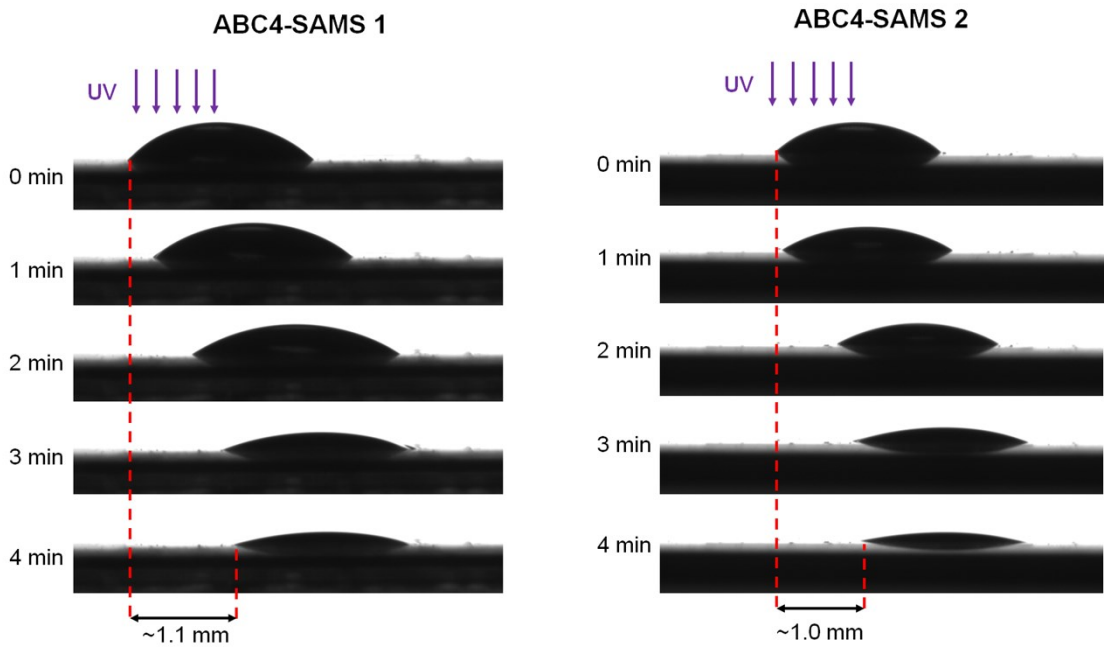

Figure S12. The UV light-driven directional measurable movement of water droplet (1 μL) on two ABC4-SAMs samples.

10. Cycle experiments of water droplet movement

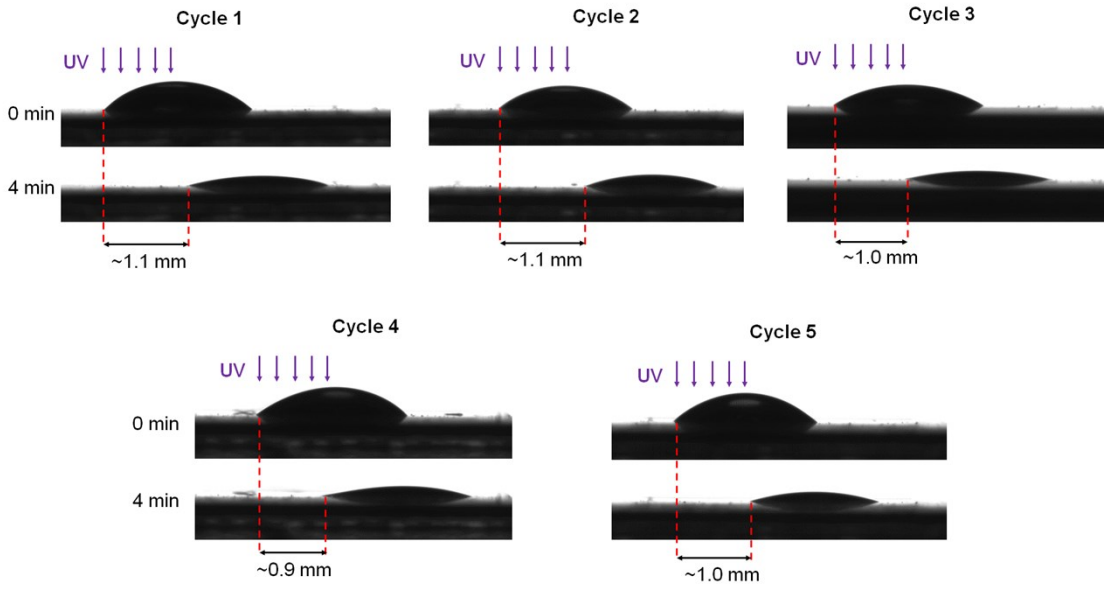

Figure S13. The cycle experiments of water droplet movement on ABC4-SAMs under asymmetric UV light irradiation.

11. References

S1. X. Zhang, H. Zhao, X. Cao, N. Feng, D. Tian and H. Li, *Org. Biomol. Chem.*, **2013**, *11*, 8262–8268.

S2. Y. Morita and T. Agawa, *J. Org. Chem.*, **1992**, *57*, 3658−3662.

S3. M. Żenkiewicz, *J. Achiev. Mater. Manuf. Eng.*, **2007**, *24*, 137−145.

S4. S. Zhang, J. Huang, Z. Chen, S. Yang and Y. Lai, *J. Mater. Chem. A*, **2019**, *7*, 38–63.

S5. M. K. Chaudhury and G. M. Whitesides, *Science*, **1992**, *256*, 1539–1541.