

Supplementary Information

A Photo-Responsive Macroscopic Switch Constructed by Chiral Azo-Calix[4]arene Functionalized Silicon Surface

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1. Materials and Characterization.

Useless otherwise state, all the chemicals used analytical grade and all the solutions were prepared with deionized water. R/S-phenylethylamine and propargylic bromide were purchased from Beijing nuokai Chemical factory, China. Sodium methoxide, natriumpara-aminobenzoicum and anhydrous sodium ethoxide were purchased from Sinopharm Group Chemical factory, China.

UV-vis spectra were acquired on a Lambda 900 UV/vis/NIR spectrometer (America). ¹H/¹³C NMR spectra were recorded on Varian Mercury Plus 400 instrument (America) at ambient temperature with TMS as the internal standard. ESI-MS was recorded on a Finnigan LCQ-Advantage instrument. XPS images were obtained using a PHI Quantera SXM instrument (America). The static contact Angle was measured at 25 °C by means of an OCA 20 contact-angle system (Dataphysics, Germany).

2. The synthesis calix[4]arene 1

Para aminobenzoic acid (0.29 g, 2.1 mmol) was dissolved in 0.36 mL concentrated HCl (diluted with 5 mL deionized water). The reaction

solution was stirred at -5°C under ice-salt baths, then 5 mL NaNO_2 (0.29 g, 4.2 mmol) solution was added dropwise to the reaction. The obtained crude product azobenzene was stand by the next reaction without further purification.

The calix[4]arene **1** (0.23 g, 0.46 mmol) was dissolved in 8 mL DMF and then anhydrous CH_3COONa (0.48 g, 5.8 mmol) and CH_3OH (5 mL) were added into the solution. The reaction mixture was stirred at -5°C under ice-salt baths and then the previous prepared azobenzene solution was added dropwise to the reaction. The orange red reaction solution was stirred for further 6 h under ice-salt baths. Finally, 0.1M HCl (50 mL) was added into and the reaction mixture was stirred at 60°C for 2h. The reaction was monitored by TLC plate and the resulting solid was collected by filtration. The crude product was washed by CH_3COOH (30 mL) and deionized water (30 mL) and then recrystallized by methyl/n-hexane to obtain a white solid calix[4]arene **1** as desired product (0.18 g, 48 %). ^1H NMR(400MHz, DMSO): δ 13.52-12.89 (br, 2H), 7.59 (s, 2H), 7.15 (d, $J=7.5\text{Hz}$, 4H), 7.00 (d, $J=7.6\text{Hz}$, 4H), 6.78 (t, $J=7.5\text{Hz}$, 2H), 4.94-4.78 (m, 4H), 4.27 (d, $J=13.0\text{Hz}$, 4H), 3.44 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.53, 157.11, 151.63, 133.52, 130.66, 129.46, 127.96, 126.10, 121.88, 80.24, 78.91, 63.99, 31.13. ESI-MS calcd for $\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_8$ 796.253, found: $m/z = 797.240 (+\text{H}^+)$.

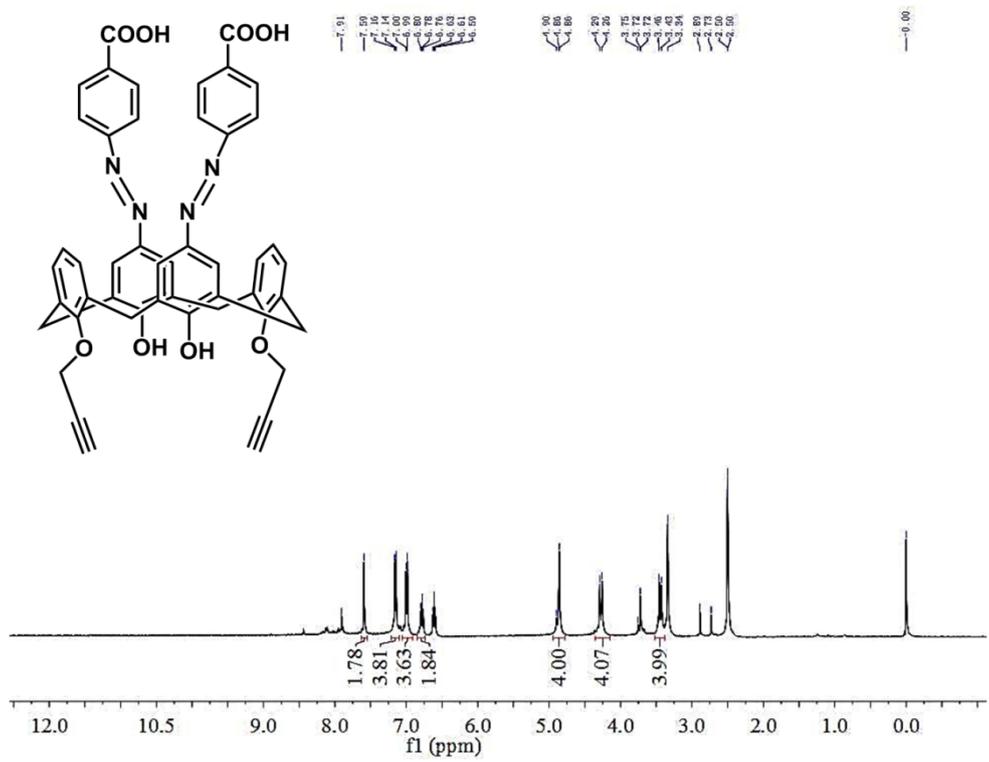


Figure S1. The ^1H NMR spectrum of calix[4]arene 1.

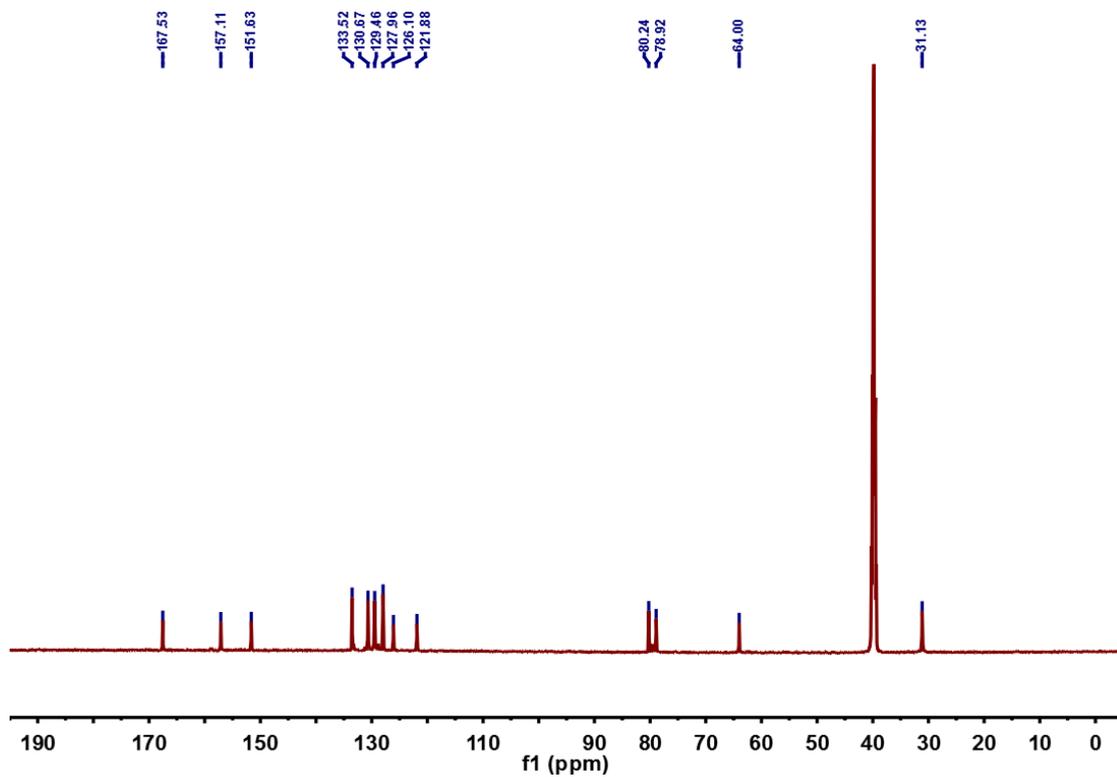


Figure S2. The ^{13}C NMR spectrum of calix[4]arene **1**.

3. The synthesis target azo-calix[4]arene FC4AD

The mixture of calix[4]arene **1** (1.0 g, 25 mmol) and HBTU (2.4 g, 6.25 mmol) in 80mL CH_2Cl_2 (re-distilled) was stirred for 5 min under N_2 atmosphere, then DIPEA (1.1 mL, 6.25 mmol) and S-phenylethylamine (1.0 mL, 7.5 mmol) were added into reaction solution. The reaction mixture was stirred for overnight and monitored by TLC plate. The reaction mixture was washed with water (50 mL) for three times and the organic fraction was dried over Na_2SO_4 and then concentrated under reduced pressure. Purification by column chromatography (petroleum: CH_2Cl_2 =1:1) of the crude residue afforded the desire product FC4AD as a white solid (0.4 g, 32 %). ^1H NMR (400 MHz, CDCl_3) δ 7.92-7.80 (m, 12H), 7.53 – 7.31 (m, 10H), 7.13 (d, $J = 7.0$ Hz, 2H), 6.97 (d, $J = 7.4$ Hz, 4H), 6.78 (t, $J = 7.1$ Hz, 2H), 6.38 (d, $J = 7.6$ Hz, 2H), 5.51 – 5.25 (m, 2H), 4.85 (s, 4H), 4.47 (d, $J = 13.3$ Hz, 4H), 3.58 (d, $J = 13.4$ Hz, 4H), 2.65 (s, 2H), 1.65 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.87, 156.82, 154.46, 151.08, 145.55, 142.88, 135.18, 132.43, 129.32, 128.64, 128.40, 127.80, 127.38, 126.02, 125.59, 124.06, 122.33, 63.55, 49.24, 31.64, 21.59. ESI-MS calcd for $\text{C}_{64}\text{H}_{54}\text{N}_6\text{O}_6$ 1002.410, found: $m/z = 1025.680$ (+ Na^+).

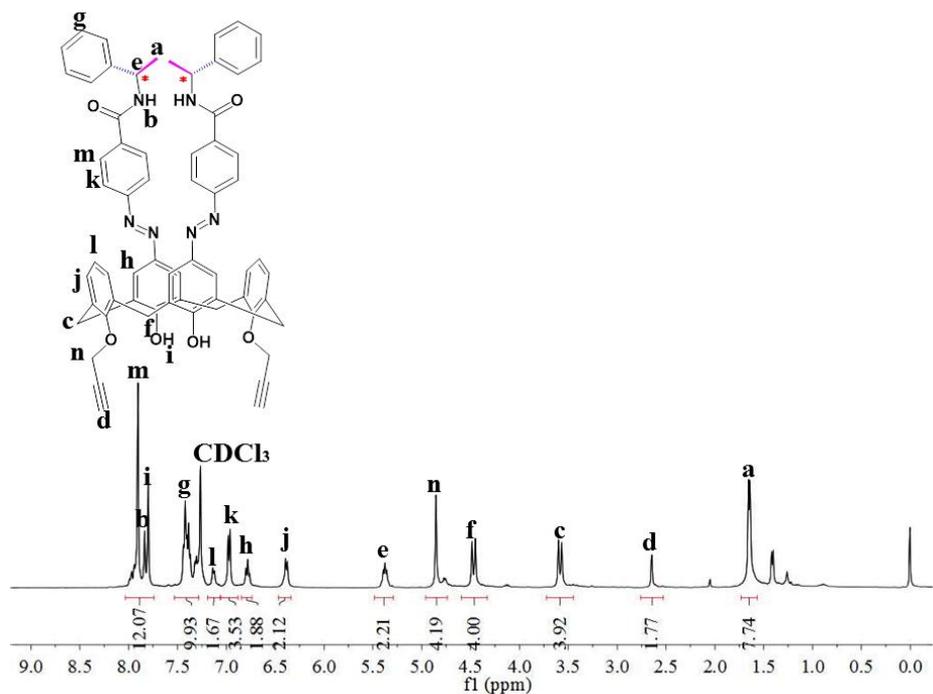
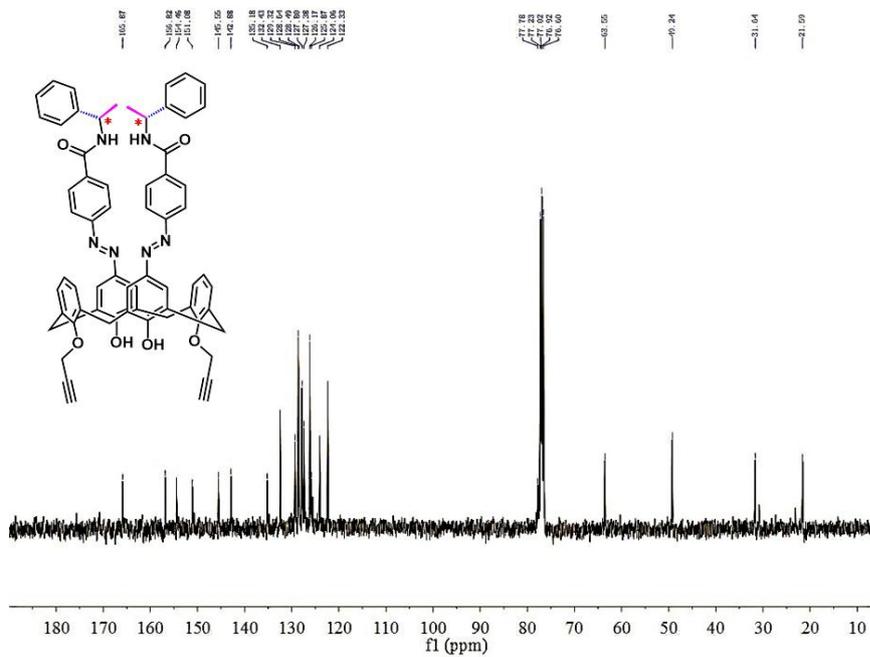


Figure S3. The ^1H NMR spectrum of FC4AD.



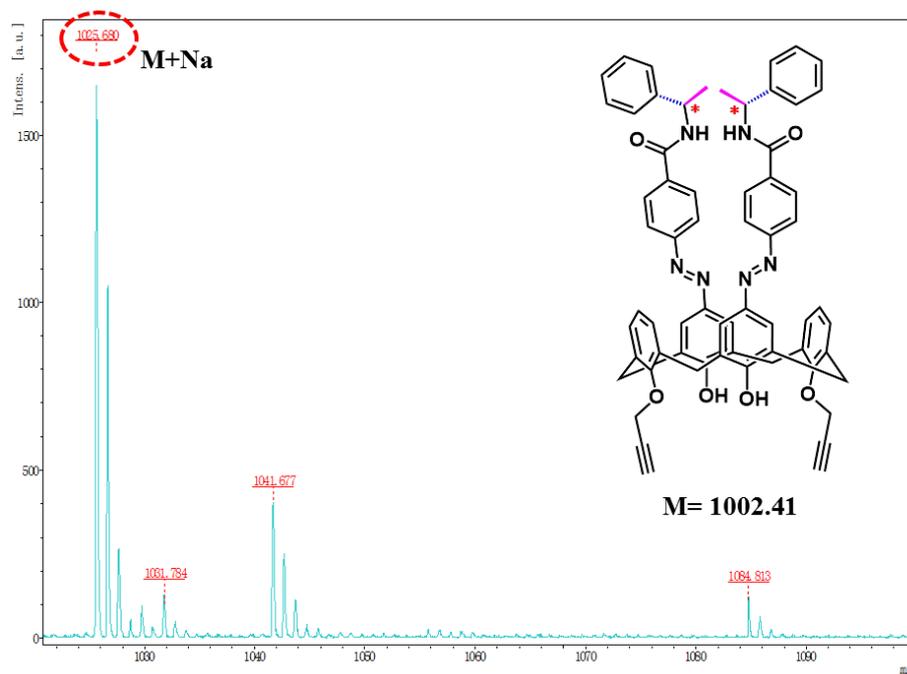


Figure S5.The ESI-MS of FC4AD.

4. The FC4AD binding with G1 in the solution

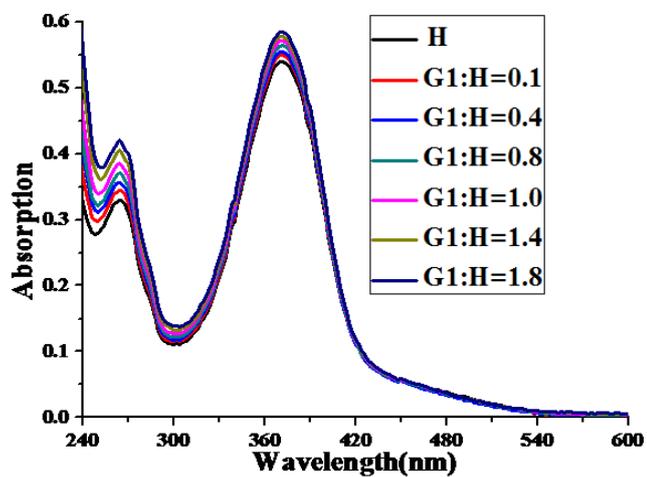


Figure S6. UV-vis spectrum of different molar ratio of FC4AD and G1

5. The FC4AD binding with G2 in the solution

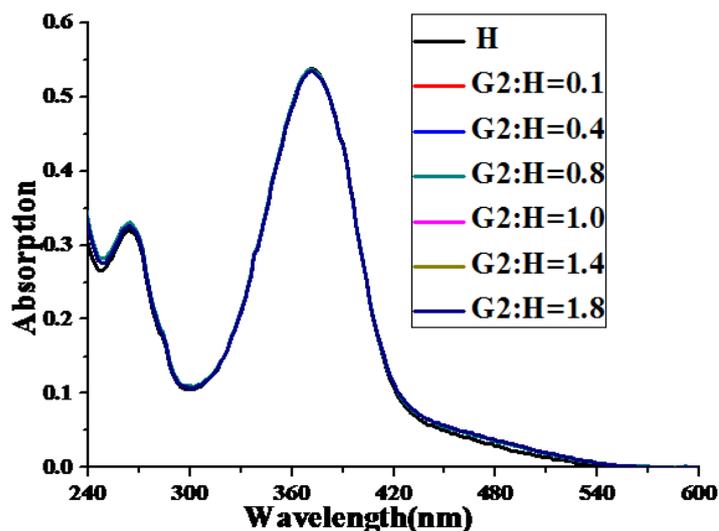


Figure S7. UV-vis spectrum of different molar ratio of FC4AD and G2

6. The experimental for photoisomerization

The irradiation light source for photoisomerization was a 300 W xenon lamp equipped with 365 and 450 nm cutoff filters ($E = 1000 \text{ mW cm}^{-2}$), respectively, and the distance between the UV lamp and the sample was about 20 cm. The samples were irradiated under UV light (365 nm) illumination at room temperature for 20 min and irradiated under visible light (450 nm) illumination for 1 h.

7. The cycling experiment of the UV-Vis spectra of photo-responsive FC4AD binding/release with G1 in the solution

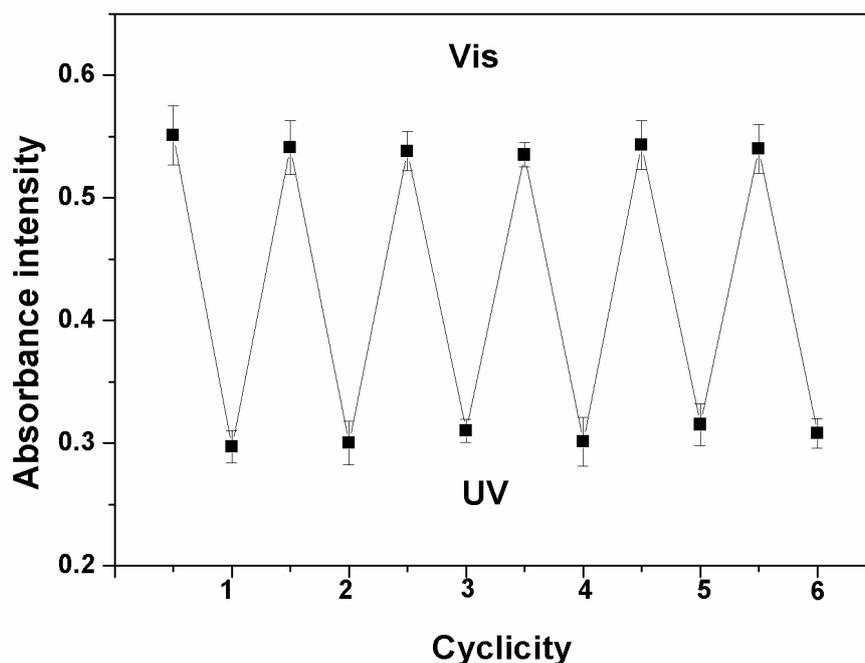


Figure S8. The Cycling experiment of the UV-Vis spectra of photo-responsive FC4AD binding/release with G1 in the solution

8. The Gaussian calculation of FC4AD+G1 and FC4AD+G2

DFT computational details. The calculations reported in this article were performed using Gaussian03 program package. The structure of the complex of FC4AD, G1 and G2 have been optimized by going through a cascade process starting from HF/3-21G R HF/6-31G R B3LYP/3-21G R B3LYP/6-31G. The frequency analysis calculations were performed and the absence of imaginary frequencies indicated the low energy minimum of the structures obtained.

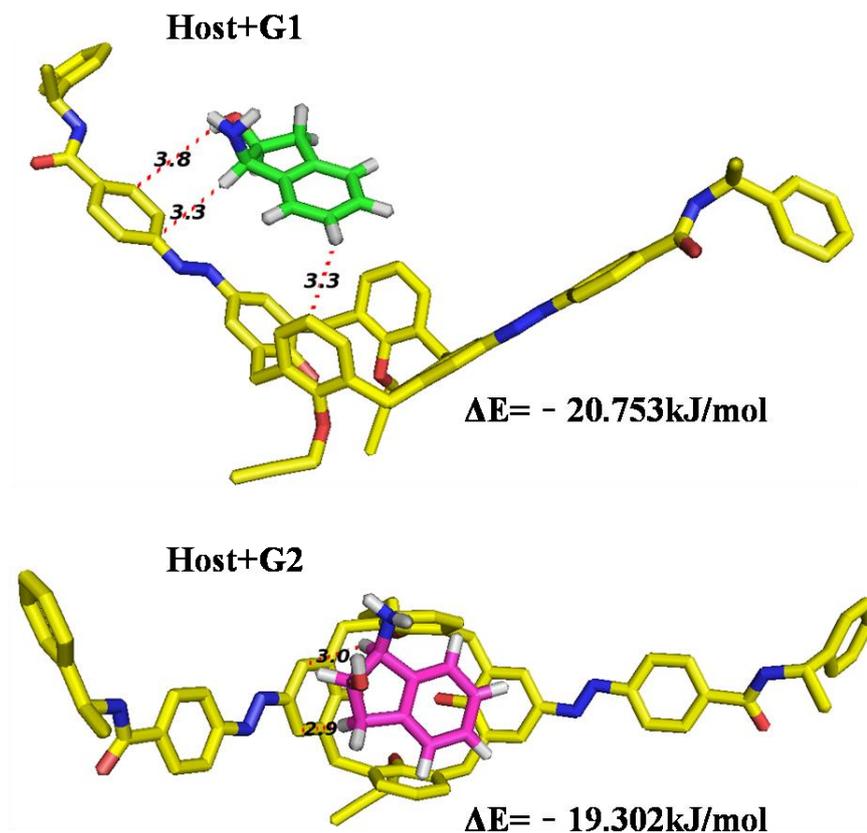
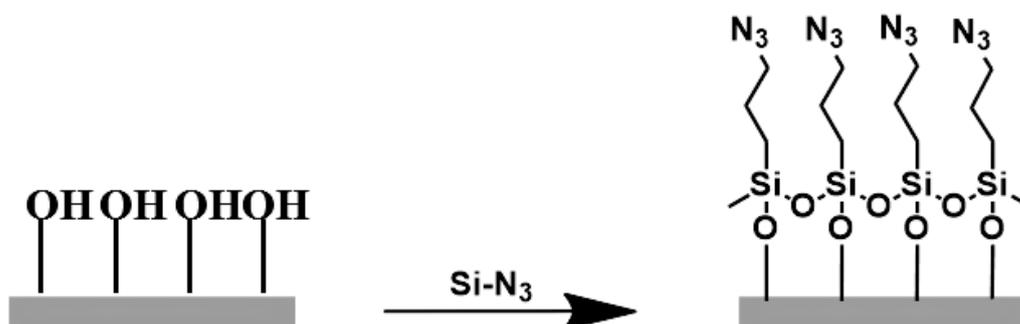


Figure S9. The Gaussian calculation of binding energy of FC4AD+G1 and FC4AD+G2

9. Modified the silicon surface with Si-N₃



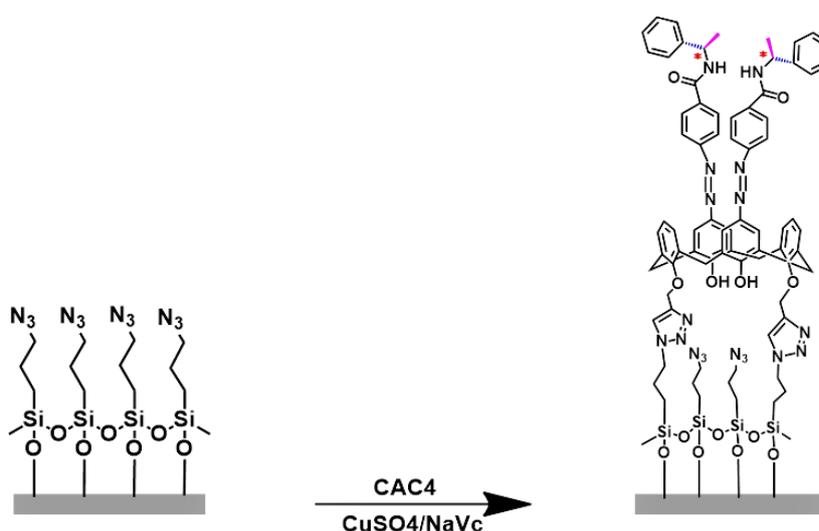
Scheme S1. Modified the silicon slice with Si-N₃

As shown in scheme S1, the etched silicon slice was immersed in a refluxed solution of 5 % Si-N₃ in dry toluene solution (10 mL) at 90°C for 8 h. Then the treated silicon slice was taken out and washed by toluene

and chloroform to remove excess Si-N₃ and dried under a stream of N₂ gas. The desired Si-N₃ surface was further characterized by contact angle (CA) and X-ray photoelectron spectroscopy (XPS).

10. Preparing the FC4AD modified Si-N₃ surface by Cu catalyzed Click Chemistry

As shown in scheme S2, the silicon surfaces modified Si-N₃ was immersed in FC4AD ethanol solution (10⁻³ M), then the mixture of copper sulfate (10⁻⁶ M) and sodium ascorbate (10⁻⁷ M) were added into reaction solution. The reaction mixture was stirred at 50°C for 8 h under click reaction. Finally, the treated Si-N₃ surface was wash with little CH₃CN and dried under a stream of N₂ to obtain the FC4AD functional Silicon surface. The FC4AD modified Si-N₃ surface was further characterized by contact angle and XPS.



Scheme S2. FC4AD modified Si-N₃ surface by Cu catalyzed Click Chemistry

11. CA relationship for FC4AD modified surface with G2 and

irradiated by UV

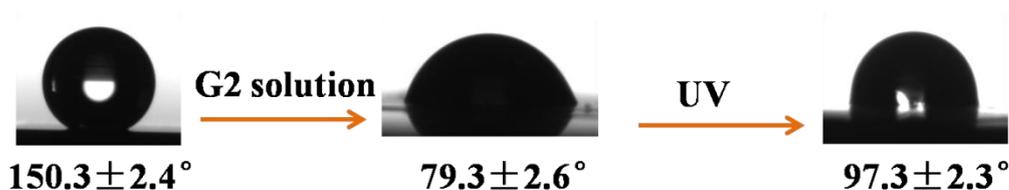


Figure S10. CA relationship for FC4AD modified surface with G2 and irradiated by UV

12. The XPS spectrum of the Si-N₃ surface before and after FC4AD modification

As shown in Figure S4, Si-N₃ surface contained 3.63% nitrogen before FC4AD modified. After the FC4AD modification, the nitrogen increased 5.7%. This result certified the successfully FC4AD modification on the silicon surface.

(a)

Name	Start BE	Peak BE	End BE	eight Count	FWHM eV _{3a}	(P) CPS.	Area (N)	At. %
C1s	290.25	284.64	281.45	21489	2.57	62344	24541	44.17
O1s	535.65	532.19	529.1	98327	1.92	210940	29001	52.2
N1s	404.5	400.05	397.2	3211.4	2.53	9136.6	2018.3	3.63

(b)

Name	Start BE	Peak BE	End BE	eight Count	FWHM eV _{3a}	(P) CPS.	Area (N)	At. %
C1s	290.55	284.6	281.1	21702	2.67	65305	25707	31.57
O1s	535.5	532.15	529.1	98237	1.98	213271	29321	36.01
N1s	406.7	400.26	396.1	7352.7	2.64	21023	4644.3	5.7

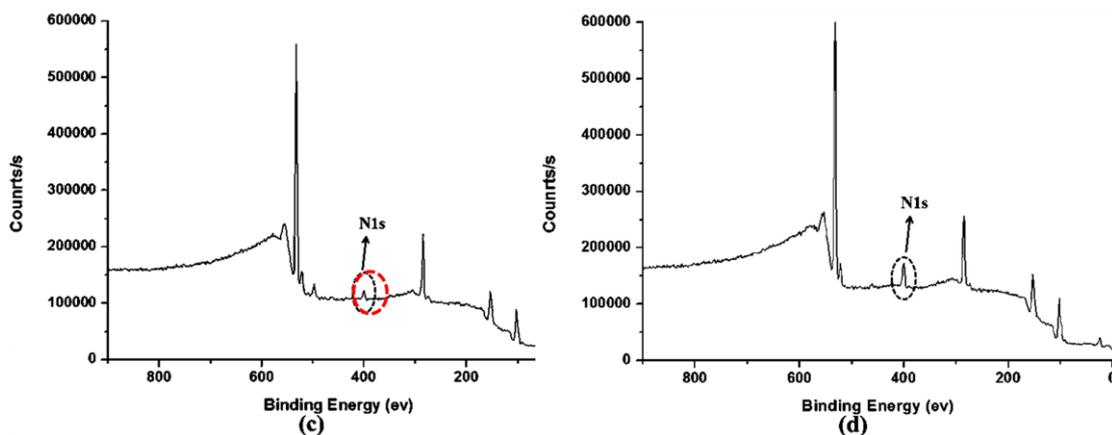


Figure S11. The XPS spectra of Si-N₃ surface before and after FC4AD

modification.

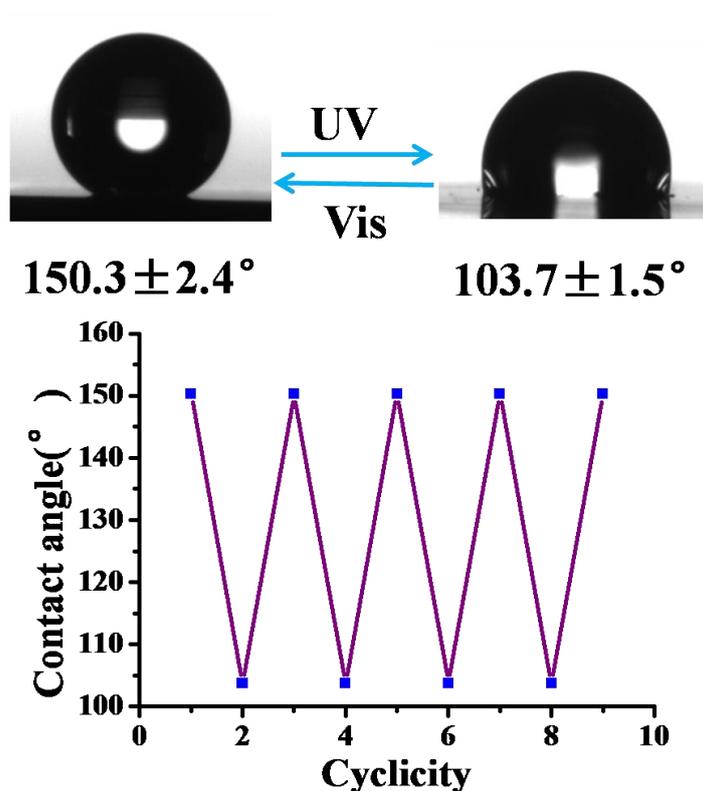


Figure S12. The Cycling experiment of respective CA change in wettability during the FC4AD modified surface regulated by photo-irradiation

13. References

- [1] Collins, E. M.; Mckerverey, M. A.; Madigan, E.; et al. *J. Chem. Soc. Perkin Trans.* **1991**, *1*, 3137-3142.