Electronic Supplementary Information

Orthogonal Photo-switching of Supramolecular Patterned Surfaces

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1. Materials

2-nitroresorcinol ($C_6H_5NO_4$, CAS No. 601-89-8), 2-iodopropane (C_3H_7I, CAS No. 75-30-9), phloroglucinol ($C_6H_6O_3$, CAS No. 108-73-6), 2-bromopopane ($C3H_7Br$, CAS No. 75-26-3), tin (II) chloride dihydrate ($SnCl_2$ $2H_2O$, CAS No. 10025-69-1), and 4-phenylazophenol ($C_{12}H_{10}N_2O$, CAS No. 1689-82-3) were purchased from Alfa Aesar. 1-Heptanol ($C_7H_{16}O$, CAS No. 111-70-6), (3-isocyanatopropyl) triethoxysilane (3-ICPES) ($C_{10}H_{21}NO_4Si$, CAS No. 24801-88-5), trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane ($C_8H_4C_{l3}F_{13}Si$, CAS No. 78560-45-9), fluorescein isothiocyanate (FITC) ($C_{21}H_{11}NO_5S$, CAS No. 3326-32-7), and rhodamine B (RhB)

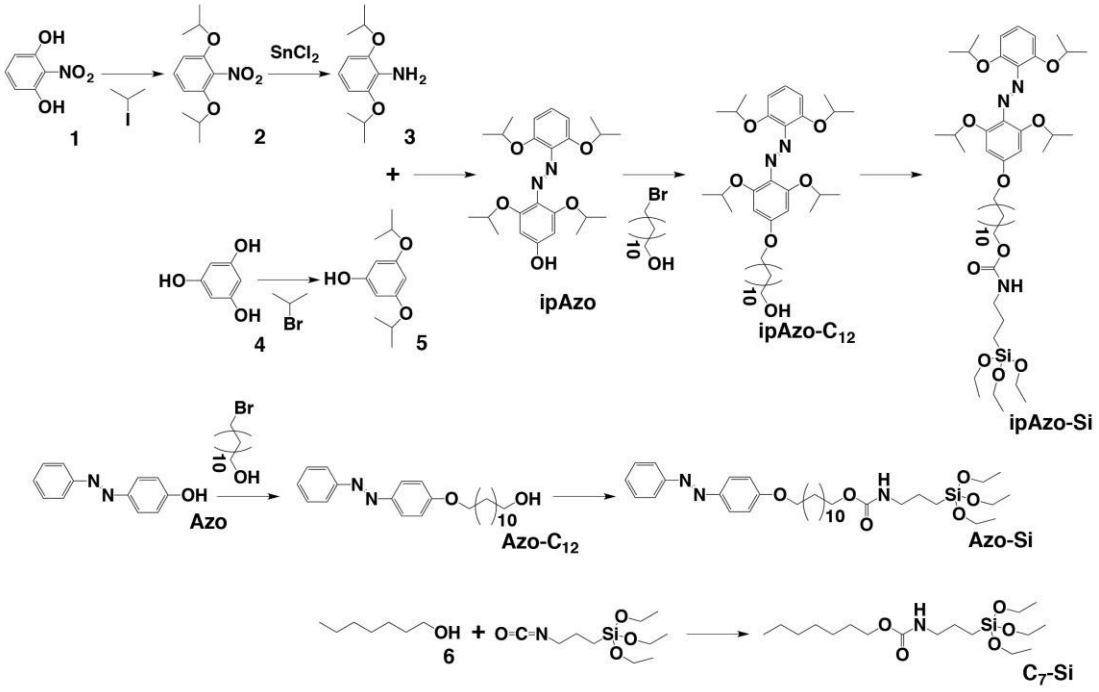
($C_{28}H_{31}ClN_2O_3$, CAS No. 81-88-9) were purchased from Sigma Aldrich. 3A-Amino-3A-deoxy-(2AS, 3AS)-α-cyclodextrin (α-CD-NH_2) ($C_{36}H_{61}NO_{29}$, CAS No. 121916-94-7), 3A-Amino-3A-deoxy-(2AS, 3AS)-γ-cyclodextrin (γ-CD-NH_2) ($C_{48}H_{81}NO_{39}$, CAS No. 189307-64-0), and 12-bromo-1-dodecanol ($C_{12}H_{25}BrO$, CAS No. 3344-77-2) were purchased from TCI GmbH. N-(3-dimethylaminopropyl)- N`-ethylcarbodiimide hydrochloride (EDC) ($C_8H_{18}N_3Cl$, CAS No. 25952-53-8) was purchased from Acros Organics. Polydimethylsiloxane (PDMS) was purchased from Dow Corning (Sylgard 184). SU-8 photoresist was purchased from MicroChem. P-type silicon wafers were purchased from Crystec Kristalltechnologie. Photolithography masks were purchased from Compugraphics Jena. High precision microscope cover glasses were purchased from Carl Roth GmbH. All the solvents (HPLC grade) were purchased from Sigma Aldrich and were directly used without any further purification. Milli-Q water (resistivity: 18.2 MΩ×cm) provided by a Sartorius Arium 611 VF Purification System was used throughout the project.

2. Methods

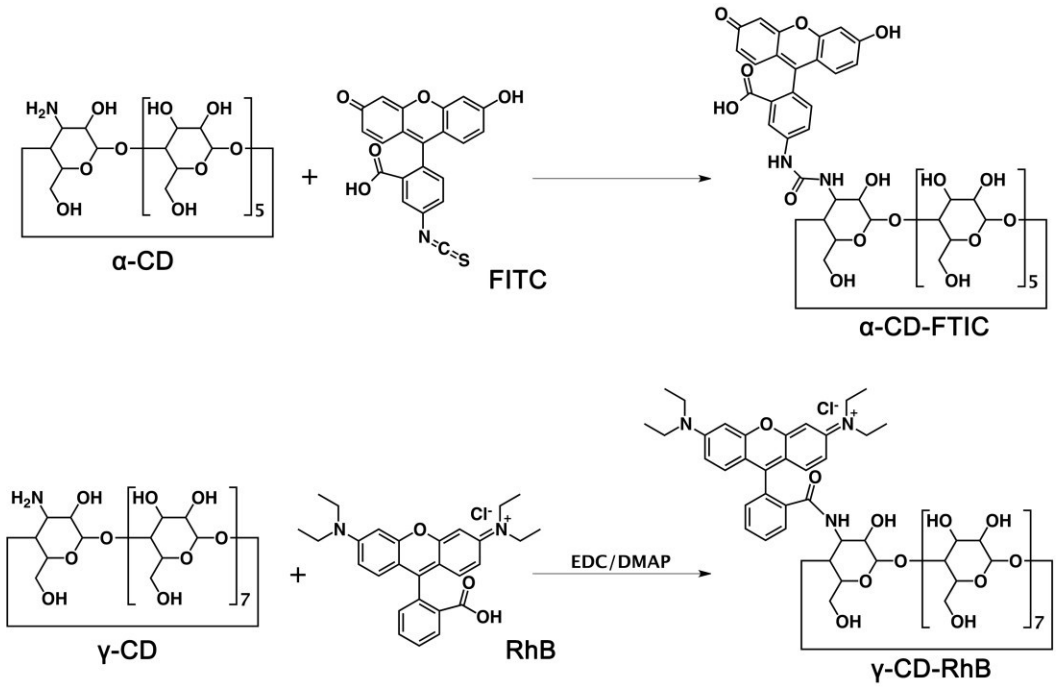
^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 MHz spectrometer. Mass spectra (MS) were obtained using a VG instrument ZAB 2-SE-FPD. Elemental analyses (C, H, and N) were tested on a CARLO ERBA 1106 elemental analyzer, with a carrier gas (He, at a flow rate of 100 mL/min) at a combustion temperature of 1000 ^{o}C using solid samples. UV/vis absorption spectra were measured on a Lambda 900 spectrometer (Perkin Elmer). Photolithography was carried out as directed by the manufacturer for 10 μm pattern heights on a MJB 3 UV 400 mask aligner (Süss Microtec Lithography) equipped with a PL-360 LP filter (Omega Optical). The images of PDMS stamp were recorded on a nanofocus μsurf system. The micropatterns were investigated by an inverted confocal microscope Leica TCS SP8 SMD. Laser line 458 nm was used for reflection of the substrate, laser lines 488 and 561 nm were used for excitation of FITC and RhB. The detection range for FITC and RhB were 493-544 nm and 566-613 nm. Photoisomerization was induced by LEDs with the wavelengths of 365, 470, 530 and 625 nm (device types LCS-0365-03-22, LCS-0470-03-22, LCS-0530-03-22, and LCS-0625-03-22, Mightex Systems). The output intensities of the LEDs were controlled by an LED controller (device type SLC-MA04-MU, Mightex Systems) and were calibrated by an optical powermeter (Model 407A, Spectra-Physics Corporation).

3. Synthesis

The synthetic route of the chemicals is show in **Scheme S1** and **Scheme S2**.



Scheme S1. Route for the synthesis of the chemicals.



Scheme S2. Route for the synthesis of α-CD-FITC and γ-CD-RhB.

Synthesis of 2. The synthesis of 2 is according to our published work [1]. 2-nitroresorcinol (1 in **Scheme S1**, 1550 mg, 10 mmol), 2-iodopropane (3910 mg, 23 mmol) and K_2CO_3 (4140 mg, 30 mmol) were dissolved into 100 mL of DMF. After stirring under 90 ºC for 16 h, the DMF was removed by roto-evaporation. The residue was washed by ethyl acetate (EA) 3 times to obtain the rough product. The black solid was further purified by chromatography using dichloromethane as eluent to obtain product 2.

Synthesis of 3. The synthesis of 3 is according to our published work [1]. 2 (2300 mg, 10 mmol) and excess of $SnCl_2\,2H_2O$ (4500 mg, 20 mmol) were dissolved into 30 mL of EA. The mixture was kept stirring under 60 ºC for 20 h. Then the mixture was poured into excess saturated Na_2CO_3 aqueous solution and a copious white precipitate was formed immediately. The precipitate was filtrated and the clear solution was washed with EA 3 times to obtain the rough product. The oil-like product was further purified by chromatography using dichloromethane as eluent to obtain the product 3.

Synthesis of 5. The synthesis of 5 is according to our published work [1]. 4 (1260 mg, 10 mmol), 2-bromopropane (7320 mg, 60 mmol), K_2CO_3 (8280 mg, 60 mmol) and KI (400 mg, 2.4 mmol) were dissolved into 100 mL of DMF. The reaction was kept stirring under 90 ºC for 48 h. Then the DMF was removed by roto-evaporation and the residue was washed by EA 3 times to obtain the rough product. The black oil-like rough product was further purified by chromatography using dichloromethane/methanol (10:1) as eluent to obtain product 5.

Synthesis of ipAzo. The synthesis of ipAzo is according to our published work

[1]. 3 (823 mg, 3.9 mmol) was dissolved in the mixture of 0.75 mL of H_2O and 0.97 mL of HCl (37 *wt. %*). After the solution was cooled to 0~5 ºC, $NaNO_2$ (276 mg, 4.0 mmol) in 4 mL H_2O was added quickly. The solution was stirred for 20 min and the temperature of the solution was kept 0~5 ºC. 5 (823 mg, 3.9 mmol) and NaOH (300 mg, 7.5 mmol) were dissolved in 3 mL of H_2O and then the mixture was added slowly in the diazonium salt solution at 0~5 ºC. After stirring overnight the dark red solid was collected and purified by chromatography using EA/THF (1:1) as eluent to obtain the product ipAzo. There were still plenty of ipAzo dispersed in the H_2O phase, using EA to wash it could increase the yield.

Synthesis of ipAzo-C_{12}. ipAzo (430 mg, 1.0 mmol), 12-bromo-1-dodecanol (291 mg, 1.1 mmol), K_2CO_3 (152 mg, 1.1 mmol), and KI (20 mg, 0.1 mmol) were dissolved in 20 mL of DMF. The mixture was kept stirring under 90 ºC overnight. Then the DMF was removed by roto-evaporation, and the residue was washed by EA 3 times to obtain the rough product. The red solid was further purified by chromatography using dichloromethane as eluent to obtain ipAzo-C_{12}. Yield: 90%. ^{1}H NMR (DMSO-*d6*, 300 MHz): δ=7.14 (t, J=8.3 Hz, 1H), δ=6.73 (d, J=8.4 Hz, 2H), δ=6.31 (s, 2H), δ=4.54 (ddt, J=26.9, 12.0, 6.0 Hz, 4H), δ=4.32 (t, J=5.2 Hz, 1H), δ=4.05 (t, J=6.5 Hz, 2H), δ=1.78-1.64 (m, 2H), δ=1.49-1.23 (m, 20H), δ=1.17 (dd, J=9.8, 6.1 Hz, 24H). ^{13}C NMR (DMSO-d6, 300 MHz): δ=162.09, δ=152.31, δ=149.47, δ=135.04, δ=130.21, δ=122.71, δ=109.47, δ=95.89, δ=71.20, δ=69.45, δ=60.67, δ=32.50, δ=28.92, δ=25.47, δ=21.90, δ=21.83, δ=21.30. MS cal: m/z= 614.4 found: m/z=614.8.

Synthesis of ipAzo-Si. ipAzo-C_{12} (615 mg, 1.0 mmol) and 3-ICPES (149 mg, 1.0 mmol) were dissolved in 30 mL of THF. The mixture was heated under reflux and an atmosphere of Ar overnight. After removal of the solvent, the residue was washed by hexane 3 times to obtain ipAzo-Si. Yield: 95%. ^{1}H NMR (DMSO-*d6*, 300 MHz): δ=7.13 (t, J=8.3 Hz, 1H), δ=7.07 (s, 1H), δ=6.73 (d, J=8.4 Hz, 2H), δ=6.31 (s, 2H), δ=4.54 (ddt, J=26.9, 12.0, 6.0 Hz, 4H), δ=4.05 (t, J=6.5 Hz, 2H), δ=3.90 (t, J=6.5 Hz, 2H), δ=3.72 (q, J=6.82, 6.96, 6H), δ=2.91 (q, J=6.60, 6.63, 2H), δ=1.78-1.64 (m, 2H), δ=1.60-1.23 (m, 22H), δ=1.20-1.10 (m, 33H), δ=0.50 (m, 2H). ^{13}C NMR (DMSO-*d6*, 300 MHz): δ=162.09, δ=160.21, δ=152.31, δ=149.47, δ=137.97, δ=133.65, δ=130.17, δ=109.47, δ=95.91, δ=71.31, δ=67.70, δ=63.41, δ=57.63, δ=42.86, δ=33.95, δ=28.92, δ=25.47, δ=22.96, δ=21.90, δ=21.83, δ=21.30, δ=18.15, δ=7.11. MS cal: m/z= 861.6 found: m/z=861.2. Anal. Cald for ipAzo-Si ($C_{46}H_{79}N_3O_{10}Si$): C, 64.08; H, 9.24; N, 4.87%. Found: C, 63.85; H, 9.45; N, 4.76%.

Synthesis of Azo-C_{12}. Azo (197 mg, 1.0 mmol), 12-bromo-1-dodecanol (291 mg, 1.1 mmol), K_2CO_3 (152 mg, 1.1 mmol), and KI (20 mg, 0.1 mmol) were dissolved in 20 mL of DMF. The mixture was kept stirring under 90 ºC overnight. Then the DMF was removed by roto-evaporation, and the residue was washed by EA 3 times to obtain the rough product. The red solid was further purified by chromatography using dichloromethane as eluent to obtain Azo-C_{12}. Yield: 95%. MS cal: m/z= 382.3 found: m/z=382.2.

Synthesis of Azo-Si. Azo-C_{12} (382 mg, 1.0 mmol) and 3-ICPES (149 mg, 1.0 mmol) were dissolved in 30 mL of THF. The mixture was heated under reflux and an

atmosphere of Ar overnight. After removal of the solvent, the residue was washed by hexane 3 times to obtain Azo-Si. Yield: 93%. ^{1}H NMR (DMSO-*d6*, 300 MHz): δ=7.97-7.76 (m, 4H), δ=7.57 (m, 3H), δ=7.13 (m, 3H), δ=4.08 (t, J=6.4 Hz, 2H), δ=3.91 (t, J=6.4 Hz, 2H), δ=3.73 (q, J=7.0 Hz, 6H), δ=2.93 (q, J=6.7 Hz, 2H), δ=1.74 (q, J=6.6 Hz, 2H), δ=1.59-1.20 (m, 22H), δ=1.14 (t, J=7.0 Hz, 9H), δ=0.51 (m, 2H). ^{13}C NMR (DMSO-*d6*, 300 MHz): δ=161.47, δ=156.29, δ=151.94, δ=145.95, δ=130.76, δ=129.34, δ=124.55, δ=122.18, δ=114.97, δ=67.94, δ=63.43, δ=60.67, δ=57.63, δ=42.84, δ=28.94, δ=28.71, δ=28.53, δ=25.42, δ=22.97, δ=18.16, δ=7.08. MS cal: m/z= 629.4 found: m/z=629.4. Anal. Cald for Azo-Si ($C_{34}H_{55}N_3O_6Si$): C, 64.83; H, 8.80; N, 6.67%. Found: C, 65.27; H, 9.21; N, 6.38%.

Synthesis of C_7-Si. 6 (116 mg, 1.0 mmol) and 3-ICPES (149 mg, 1.0 mmol) were dissolved in 30 mL of THF. The mixture was heated under reflux and an atmosphere of Ar overnight. The solvent was removed by roto-evaporation to obtain C_7-Si. Yield: 97%. ^{1}H NMR (DMSO-*d6*, 300 MHz): δ=7.06 (s, 1H), δ=3.93 (t, J=6.9 Hz, 2H), δ=3.73 (q, J=7.0 Hz, 6H), δ=2.92 (q, J=6.8 Hz, 2H), δ=1.46 (m, 4H), δ=1.26 (m, 8H), δ=1.14 (t, J=7.0 Hz, 9H), δ=0.86 (m, 3H), δ=0.51 (m, 2H). ^{13}C NMR (DMSO-*d6*, 300 MHz): δ=156.27, δ=63.40, δ=57.62, δ=42.86, δ=31.17, δ=28.70, δ=28.33, δ=25.31, δ=22.96, δ=21.97, δ=18.12, δ=13.83, δ=7.11. MS cal: m/z= 363.2 found: m/z=383.6. Anal. Cald for C_7-Si ($C_{17}H_{37}NO_5Si$): C, 56.16; H, 10.26; N, 3.85%. Found: C, 56.49; H, 10.38; N, 3.67%.

Synthesis of α-CD-FITC. α-CD-NH_2 (972 mg, 1.0 mmol) and FITC (390 mg, 1.0 mmol) were dissolved in 20 mL of DMF. The mixture was kept stirring under 90 °C

for 24 h. After removal of the solvent by roto-evaporation, the rough product was washed by ethanol 3 times to obtain α-CD-FITC. Anal. Cald for α-CD-FITC ($C_{57}H_{72}N_2O_{35}$): C, 50.89; H, 5.40; N, 2.08%. Found: C, 50.08; H, 5.23; N, 2.11%.

Synthesis of γ-CD-RhB. γ-CD-NH_2 (1296 mg, 1.0 mmol), RhB (479 mg, 1.0 mmol), and EDC (211 mg, 1.1 mmol) were dissolved in 30 mL of DMF. The mixture was kept stirring under room temperature for 72 h. After removal of the solvent by roto-evaporation, the rough product was washed by ethanol 3 times to obtain γ-CD-RhB. Anal. Cald for γ-CD-RhB ($C_{76}H_{110}ClN_3O_{41}$): C, 51.95; H, 6.31; N, 2.39%. Found: C, 51.58; H, 6.13; N, 2.49%.

4. Calculation of UV/vis spectra for *cis* Azo and *cis* ipAzo

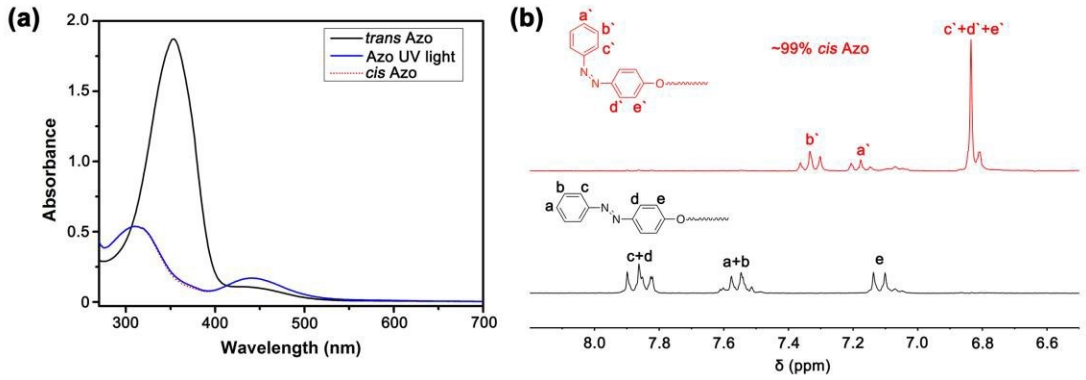


Figure S1. (a) UV/vis spectra ([Azo-Si]=0.25 mM in DMSO) of *trans* Azo before (black, solid) and after (blue, solid) UV light irradiation (60 mW/cm^2, 40 min), *cis* Azo spectrum (red, dot) was from calculation; (b) ^{1}H NMR spectra (DMSO-*d6*, 250 MHz under 298K) of *trans* Azo before (black) and after (red) UV light irradiation (60 mW/cm^2, 40 min), ~99% *cis* Azo was obtained.

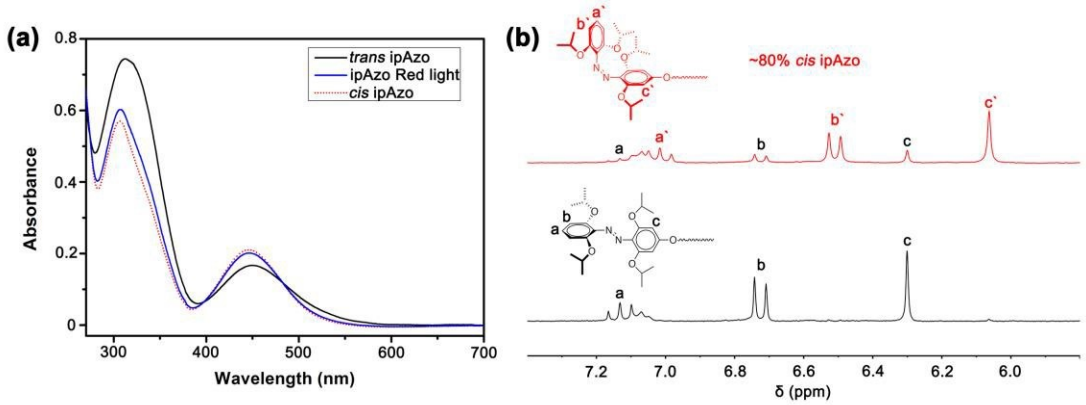


Figure S2. (a) UV/vis spectra ([ipAzo-Si]=0.25 mM in DMSO) of *trans* ipAzo before (black, solid) and after (blue, solid) red light irradiation (60 mW/cm^2, 40 min), *cis* ipAzo spectrum (red, dot) was from calculation; (b) ^{1}H NMR spectra (DMSO-*d6*, 250 MHz under 298K) of *trans* ipAzo before (black) and after (red) red light irradiation (60 mW/cm^2, 40 min), ~80% *cis* ipAzo was obtained.

The UV/vis spectrum of *cis* Azo was calculated from the UV/vis spectra of *trans* Azo and Azo after UV light irradiation.

The absorbance of Azo after UV light irradiation (A_{obs}) is,

$$A_{obs} = C_{trans} \cdot A_{trans} + C_{cis} \cdot A_{cis}$$

where C_{trans} and C_{cis} are the contents of *trans* Azo and *cis* Azo after UV light irradiation; A_{trans} and A_{cis} are the absorbance of *trans* Azo and *cis* Azo.

The A_{cis} could be therefore calculated as,

$$A_{cis} = \frac{A_{obs} - C_{trans} \cdot A_{trans}}{C_{cis}}$$

the C_{trans} and C_{cis} could be obtained from ^{1}H NMR data.

Calculation of the UV/vis spectrum of *cis* ipAzo was similar.

5. Photoisomerization of Azo and ipAzo

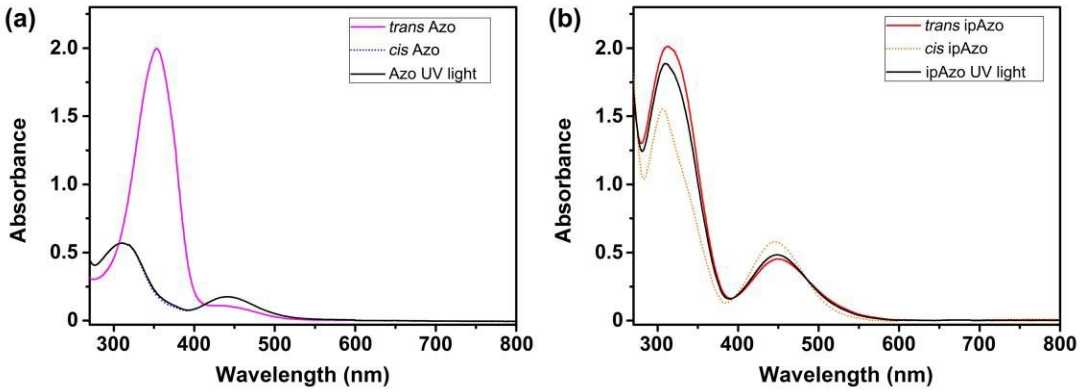


Figure S3. UV/vis spectra of Azo (a) and ipAzo (b) after UV light irradiation (365 nm, 60 mW/cm^2) for 30 min ([Azo-Si]=[ipAzo-Si]=0.25 mM in DMSO): *trans* Azo and *trans* ipAzo were obtained after heating at 60 ºC for 1 h in dark, absorbance of *trans* Azo at λ=351 nm and *trans* ipAzo at λ=310 nm were normalized; UV/vis spectra of *cis* Azo and *cis* ipAzo were obtained from calculation.

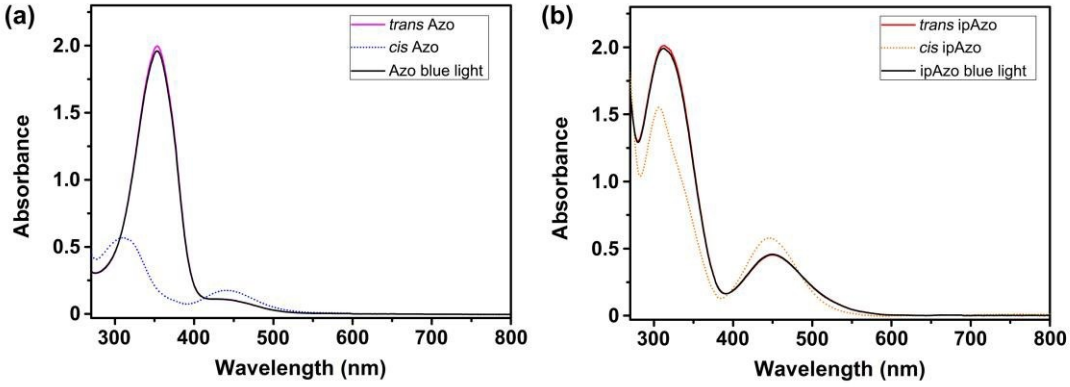


Figure S4. UV/vis spectra of Azo (a) and ipAzo (b) after blue light irradiation (470 nm, 60 mW/cm^2) for 30 min ([Azo-Si]=[ipAzo-Si]=0.25 mM in DMSO): *trans* Azo and *trans* ipAzo were obtained after heating at 60 ºC for 1 h in dark, absorbance of *trans* Azo at λ=351 nm and *trans* ipAzo at λ=310 nm were normalized; UV/vis spectra of *cis* Azo and *cis* ipAzo were obtained from calculation.

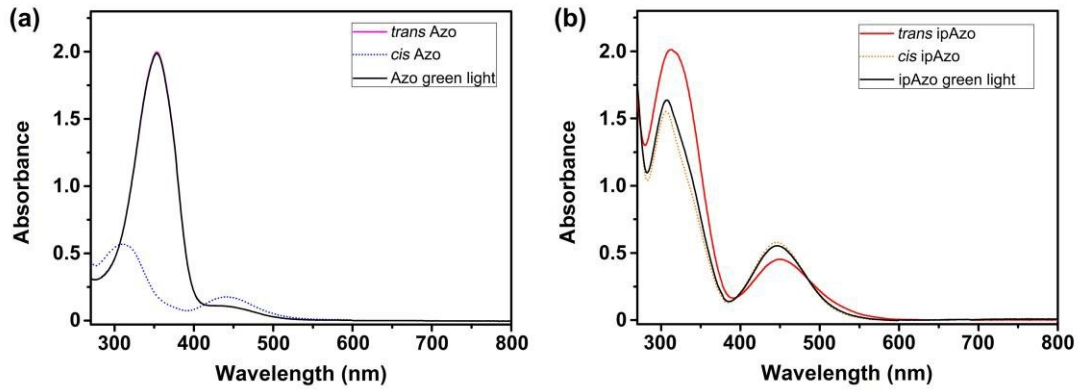


Figure S5. UV/vis spectra of Azo (a) and ipAzo (b) after green light irradiation (530 nm, 60 mW/cm^2) for 30 min ([Azo-Si]=[ipAzo-Si]=0.25 mM in DMSO): *trans* Azo and *trans* ipAzo were obtained after heating at 60 ºC for 1 h in dark, absorbance of *trans* Azo at λ=351 nm and *trans* ipAzo at λ=310 nm were normalized; UV/vis spectra of *cis* Azo and *cis* ipAzo were obtained from calculation.

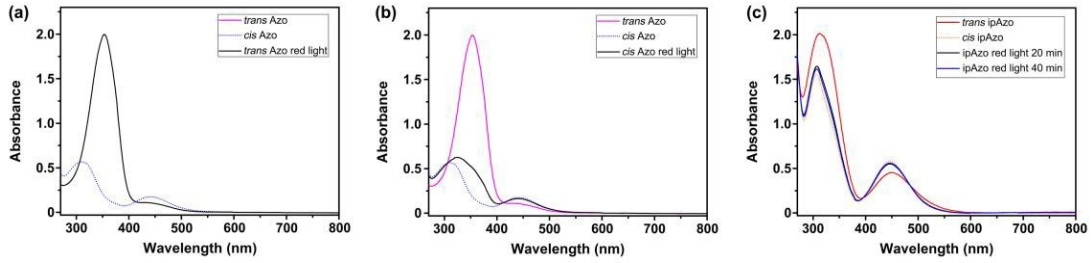


Figure S6. UV/vis spectra of *trans* Azo (a) and *cis* Azo (b) after red light irradiation (625 nm, 60 mW/cm^2) for 20 min ([Azo-Si]=0.25 mM in DMSO); (c) UV/vis spectra of ipAzo after red light irradiation (625 nm, 60 mW/cm^2) for 20 and 40 min (ipAzo-Si 0.25 mM in DMSO): *trans* Azo and *trans* ipAzo were obtained after heating at 60 ºC for 1 h in dark, absorbance of *trans* Azo at λ=351 nm and *trans* ipAzo at λ=310 nm were normalized; UV/vis spectra of *cis* Azo and *cis* ipAzo were obtained from calculation.

6. Orthogonally photo-controlled isomerization of Azo/ipAzo

The orthogonally photo-controlled isomerization of Azo/ipAzo was investigated by ^{1}H NMR, and the results are showed in the manuscript (**Figure 1(b)**).

The 3 states of *trans* Azo/*trans* ipAzo (blue light), *trans* Azo/*cis* ipAzo (green light) and *cis* Azo/*trans* ipAzo (UV light) are photostationary states, which will not be further changed with increase of the irradiation time. The isomerization of Azo and ipAzo under UV, blue and green light are very fast (<10 min), 30 min irradiation is thus long enough for the switching. The transition from *cis* Azo/*trans* ipAzo (UV light) to *cis* Azo/*cis* ipAzo (red light) is time dependent, and was investigated by ^{1}H nuclear magnetic resonance (NMR) (**Figure S7**).

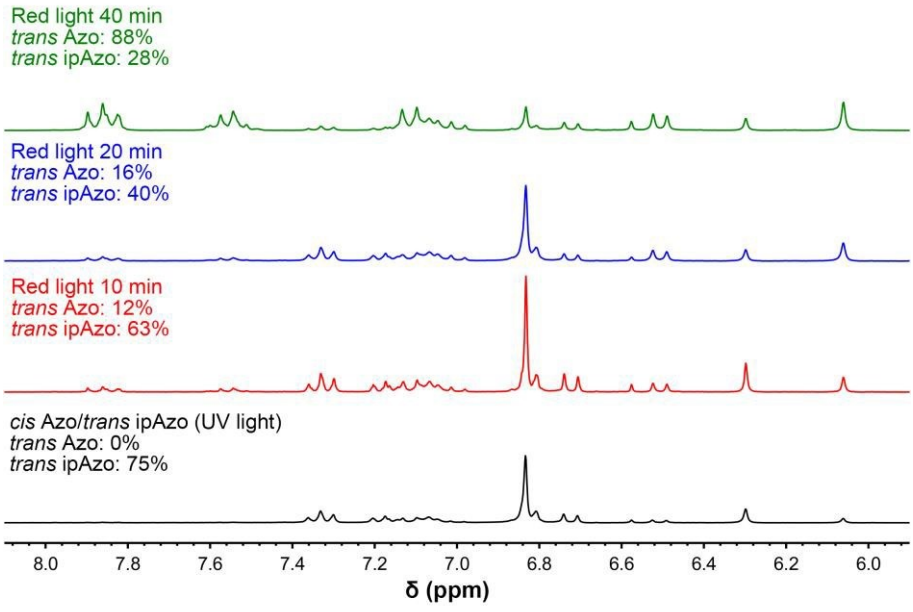


Figure S7. ^{1}H NMR spectra of Azo/ipAzo system ([Azo-Si]=[ipAzo-Si]=1.5 mM in DMSO-*d6*, 300 MHz at 298K). Red light transits *cis* Azo/*trans* ipAzo to *cis* Azo/*cis* ipAzo (60 mW/cm^2).

Started from *cis* Azo/*trans* ipAzo, the combination was irradiated by red light for 10 min, 20 min and 40 min. The *trans*-to-*cis* isomerization of ipAzo is slow under red light irradiation due to the weak absorption in this area, long time irradiation is thus needed to obtain high content of *cis* ipAzo. However, *cis* Azo is unstable and relaxes to *trans* Azo under room temperature. 10 min red light irradiation obtains only ~37% of *cis* ipAzo, which is not enough. Prolonging the irradiation time to 40 min increases the *cis* ipAzo content, however, decreases the *cis* Azo content simultaneously. Therefore, we choose 20 min irradiation time to obtain the *cis* Azo/*cis* ipAzo state.

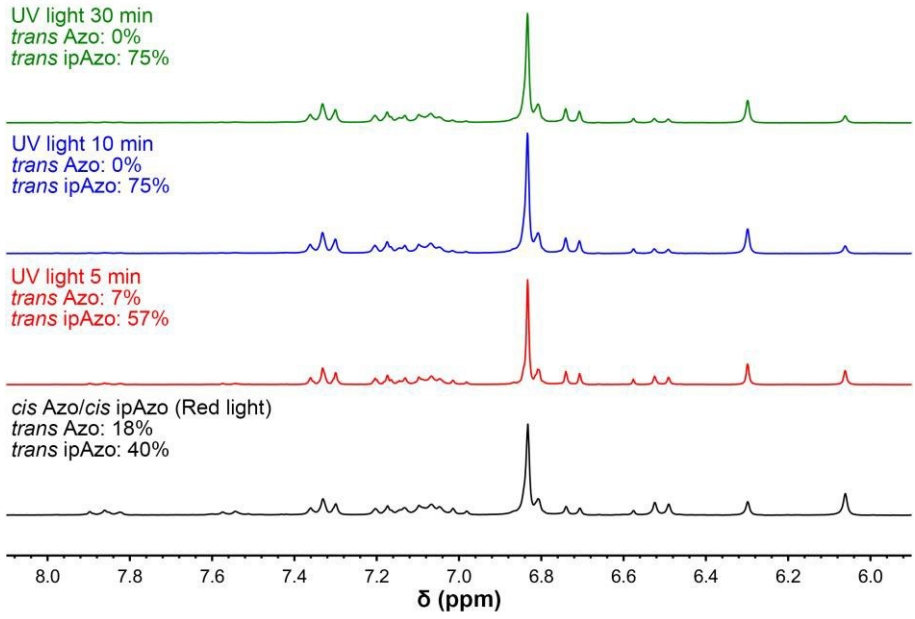


Figure S8. ^{1}H NMR spectra of Azo/ipAzo system ([Azo-Si]=[ipAzo-Si]=1.5 mM in DMSO-*d6*, 300 MHz at 298K). UV light transits *cis* Azo/*cis* ipAzo to *cis* Azo/*trans* ipAzo (60 mW/cm^2).

The transition from *cis* Azo/*cis* ipAzo (red light) to *cis* Azo/*trans* ipAzo (UV light) is time independent, due to the fast isomerization of Azo and ipAzo under UV

light irradiation (**Figure S8**). The transition is accomplished in 10 min under UV light irradiation, and the Azo/ipAzo reaches photostationary state. Longer irradiation does not make obvious change.

7. PDMS stamp

Stamps were prepared from PDMS. Firstly, a mold was fabricated by photolithography with SU-8 photoresist on silicon wafers. Afterwards, the SU-8 patterns were fluorinated by first exposing them on oxygen plasma under vacuum for 20 s and then placed in a desiccator for 1 h with ~30 mL of trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane. The substrate was then baked at 90 ºC in an oven for 1 h to complete the silanization process. The PDMS prepolymer was mixed with the crosslinking agent at a 10:1 ratio by weight in a vial and then mixed thoroughly. The liquid mixture was then degassed under vacuum, poured over the SU-8 mold, and then place into an oven at 60 ºC for ~15 h to crosslink. The solid PDMS was then carefully removed from the master and used for stamping (**Figure S9**).

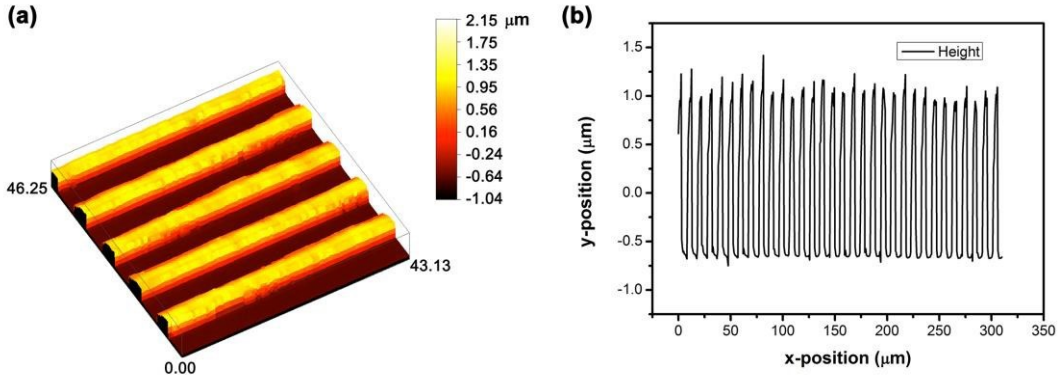


Figure S9. Nanofocus image (a) and height plots (b) of PDMS stamp surface.

8. Micropatterned surface preparation

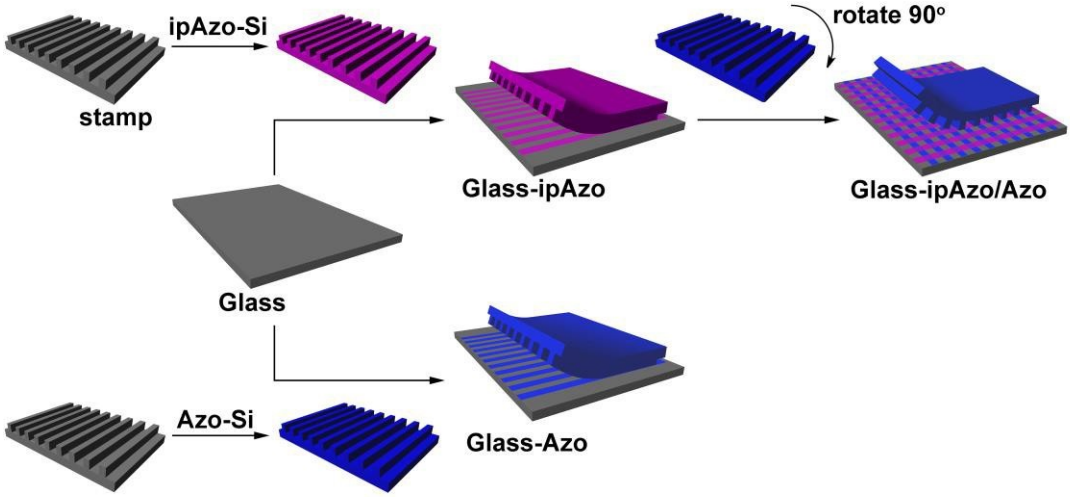
Pre-treating of glass wafer substrates. The purchased glass wafer substrates were washed by acetone, ethanol, and water sequentially. Then, the substrates were cleaned by immersing in a hot, freshly prepared piranha solution (H_2SO_4 (98%)/H_2O_2 (30%) 7:3 *v/v*) for 150 min. *Caution! Piranha solution is an extremely strong oxidant and should be handled only with the proper equipment.* The substrates were then extensively rinsed with water and dried under a flow of N_2. The substrates were immediately used in order to prevent surface contamination.

Preparation of Glass-ipAzo. As shown in **Scheme S3**, PDMS stamp was wetted by the solution of ipAzo-Si and C_7-Si ([ipAzo-Si]=0.5 mM, [ipAzo-Si]:[C_7-Si]=1:2, acetonitrile was used as the solvent) for 2 min. Then the stamp was placed on glass wafer substrate for 2.5 h under Ar atmosphere (the reaction time could be even longer if the requirement of patterned resolution is not high). After peeling away the stamp, the substrate was washed by acetone 3 times and dried under a flow of N_2 immediately to obtain Glass-ipAzo.

Preparation of Glass-Azo. The procedure is similar to the preparation of Glass-ipAzo. As shown in **Scheme S3**, PDMS stamp was wetted by the solution of Azo-Si and C_7-Si ([Azo-Si]=0.5 mM, [Azo-Si]:[C_7-Si]=1:2, acetonitrile was used as the solvent) for 2 min. Then the stamp was placed on glass wafer substrate for 2.5 h under Ar atmosphere. After peeling away the stamp, the substrate was washed by acetone 3 times and dried under a flow of N_2 immediately to obtain Glass-Azo.

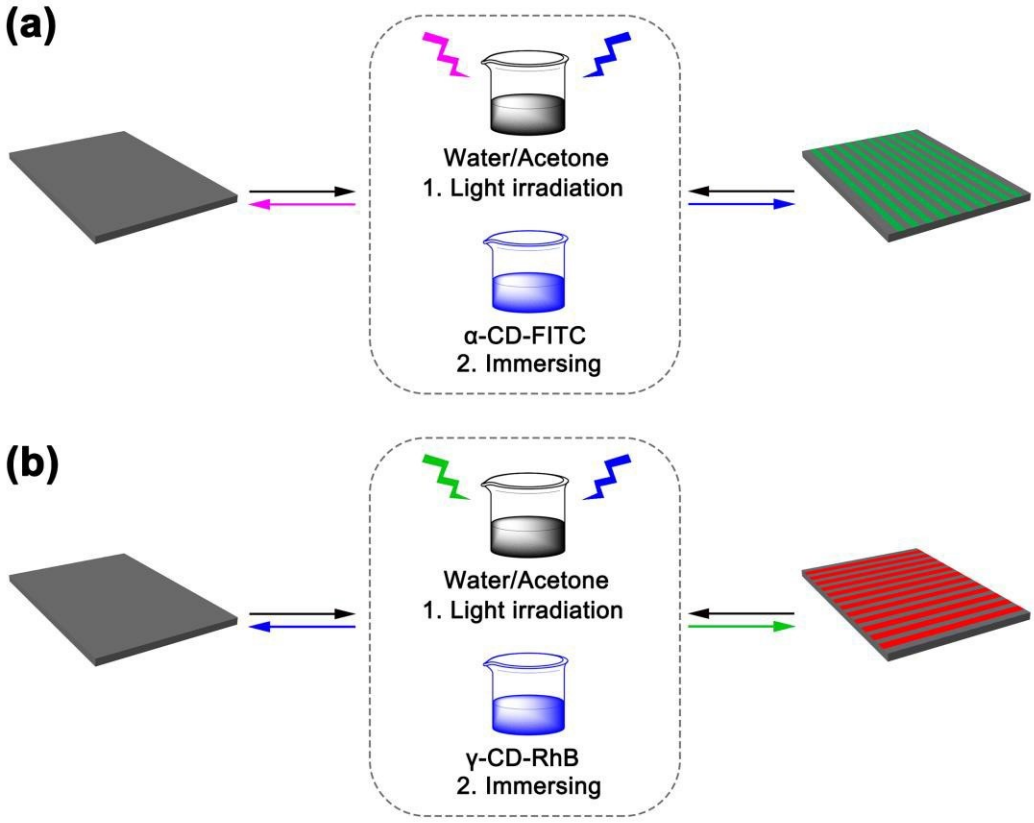
Preparation of Glass-ipAzo/Azo. Glass-ipAzo/Azo was prepared from

Glass-ipAzo (**Scheme S3**). The same PDMS stamp was wetted by the solution of Azo-Si and C_7-Si ([Azo-Si]=0.5 mM, [Azo-Si]:[C_7-Si]=1:2, acetonitrile was used as the solvent) for 2 min. Then the stamp was rotated by 90°, and placed on Glass-ipAzo for 2.5 h under Ar atmosphere. After peeling away the stamp, the substrate was washed by acetone 3 times and dried under a flow of N_2 immediately to obtain Glass-ipAzo/Azo.



Scheme S3. Schematic illustration of fabricating Glass-Azo, Glass-ipAzo and Glass-ipAzo/Azo.

9. Photo-controlling microstripes on Glass-Azo and Glass-ipAzo surface



Scheme S4. Schematic illustration of photo-controlling fluorescent microstripes on Glass-Azo (a) and Glass-ipAzo (b) surface.

Glass-Azo was immersed in α-CD-FITC solution ([α-CD-FITC]=0.1 mM, PBS buffer (pH=7.4) as the solvent) for 5 min, and then washed by water 3 times and dried under a flow of N_2. A confocal microscopy was used for the observation of the microstripes. UV light with the wavelength of 365 nm was used to "turn-off" the fluorescent microstripes (**Scheme S4 (a)**). The Glass-Azo was immersed in water/acetone (3:1 *v/v*), and irradiated by UV light for 30 min. Then the Glass-Azo was transferred into the α-CD-FITC solution and kept in dark for 5 min, followed by washing with water 3 times and drying under a flow of N_2. Blue light and heating

were applied to "turn-on" the fluorescent microstripes (**Figure S10, S11**). Glass-Azo was immersed in water/acetone under blue light irradiation for 30 min, or heating at 70 °C for 1 h.

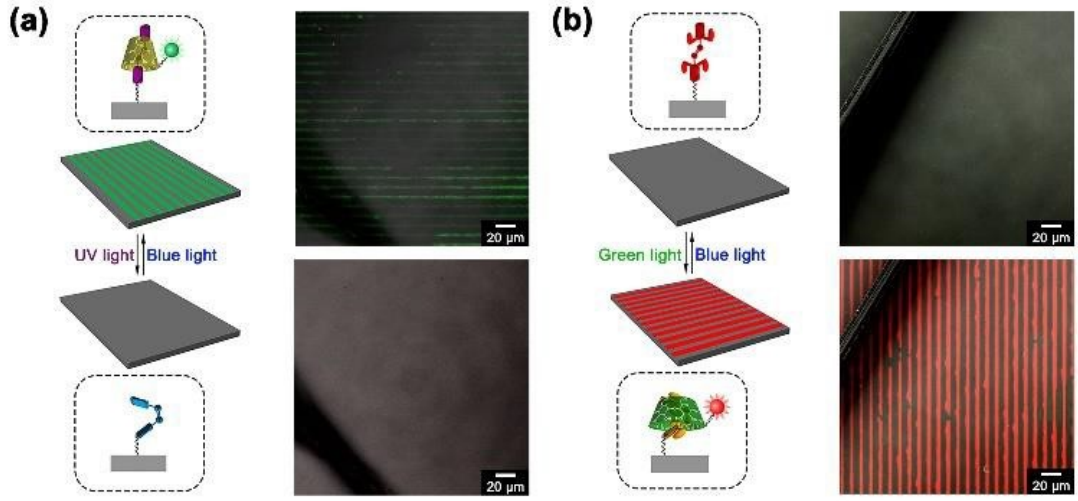


Figure S10. Confocal microscopic images of Glass-Azo (a) and Glass-ipAzo (b) after treating with various light irradiations. Both UV and blue light were used for Glass-Azo; green and blue light were used for Glass-ipAzo. The substrate surface was marked by a diamond cutter. Scale bar: 20 μm.

Glass-ipAzo was immersed in γ-CD-RhB ([γ-CD-RhB]=0.1 mM, PBS buffer (pH=7.4) as the solvent) for 5 min, and then washed by water 3 times and dried under a flow of N_2 for confocal microscopy observation. Green light with the wavelength of 530 nm was used to "turn-on" the micropatterns (**Scheme S4 (b)**). The Glass-ipAzo was immersed in water/acetone (3:1 v/v), and irradiated by green light for 30 min. After immersing in the γ-CD-RhB solution in dark for 5 min, the Glass-ipAzo was washed by water 3 times and dried under a flow of N_2. Blue light and heating could be applied to "turn-off" the micropatterns (**Figure S10, S12**). During the heating

process, the Glass-ipAzo was immersed in water and heated to 70 ºC for 1 h.

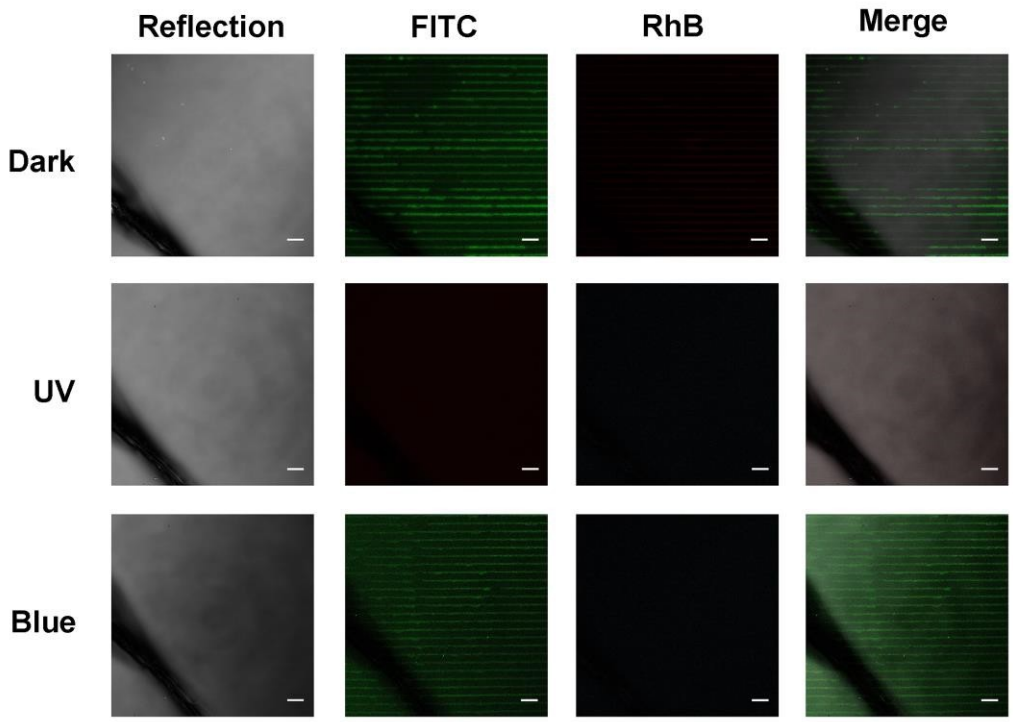


Figure S11. Confocal microscopic images of Glass-Azo after treating with UV and blue light irradiations. A mark was made on surface to make sure that the photo-switching occurred in-situ. Scale bar: 20 μm.

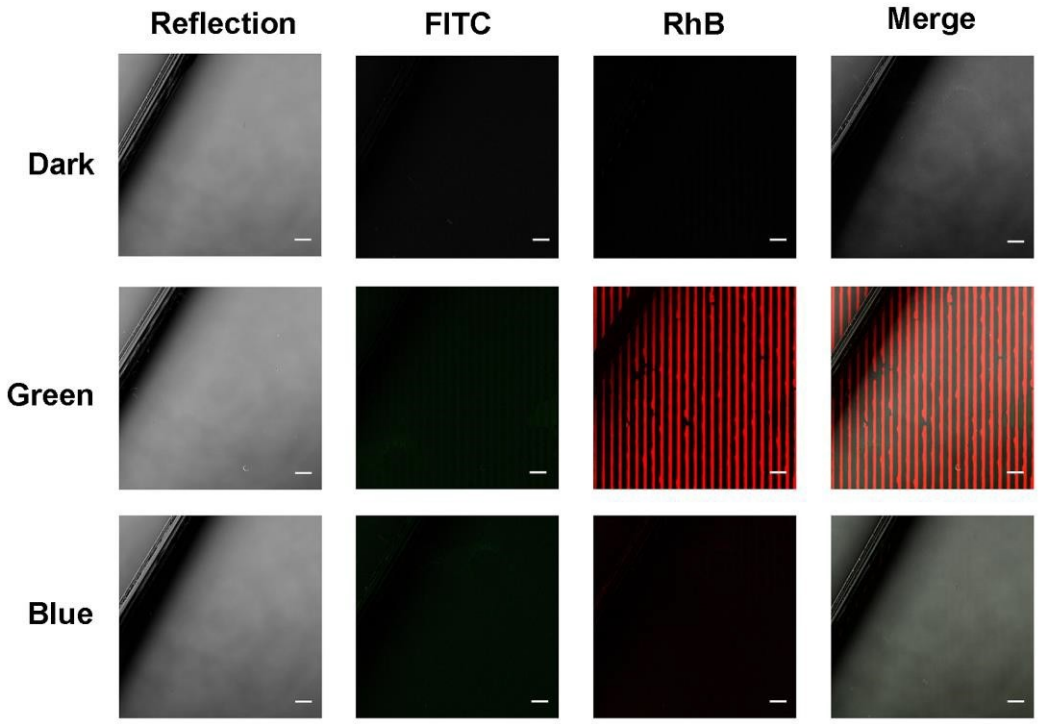
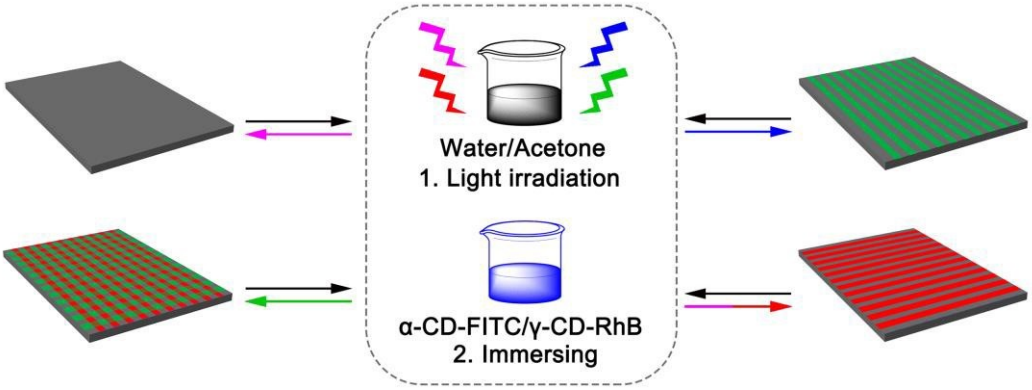


Figure S12. Confocal microscopic images of Glass-ipAzo after treating with green and blue light irradiations. A mark was made on surface to make sure that the photo-switching occurred in-situ. Scale bar: 20 μm.

10. Orthogonal photo-controlling micropatterns on Glass-ipAzo/Azo surface



Scheme S5. Schematic illustration of orthogonal photo-controlling fluorescent microstripes on Glass-ipAzo/Azo surface.

To orthogonal photo-control microstripes on Glass-ipAzo/Azo surface, a general procedure was described as follows (**Scheme S5**): For the photo-switching step, the Glass-ipAzo/Azo was immersed in water/acetone (3:1 v/v), and irradiated by light (UV, blue, green, or red) for 30 min. Then the Glass-ipAzo/Azo was transferred to mixture of α-CD-FITC and γ-CD-RhB ([α-CD-FITC]=[γ-CD-RhB]=0.1 mM, PBS buffer (pH=7.4) as the solvent) for 5 min. After washing by water 3 times and dried under a flow of N_2, a confocal microscope was used to observe the fluorescent microstripes. Heating played the similar role with blue light irradiation, during the heating process, the Glass-ipAzo/Azo was immersed in water/acetone and heated to 70 °C in the dark for 1 h.

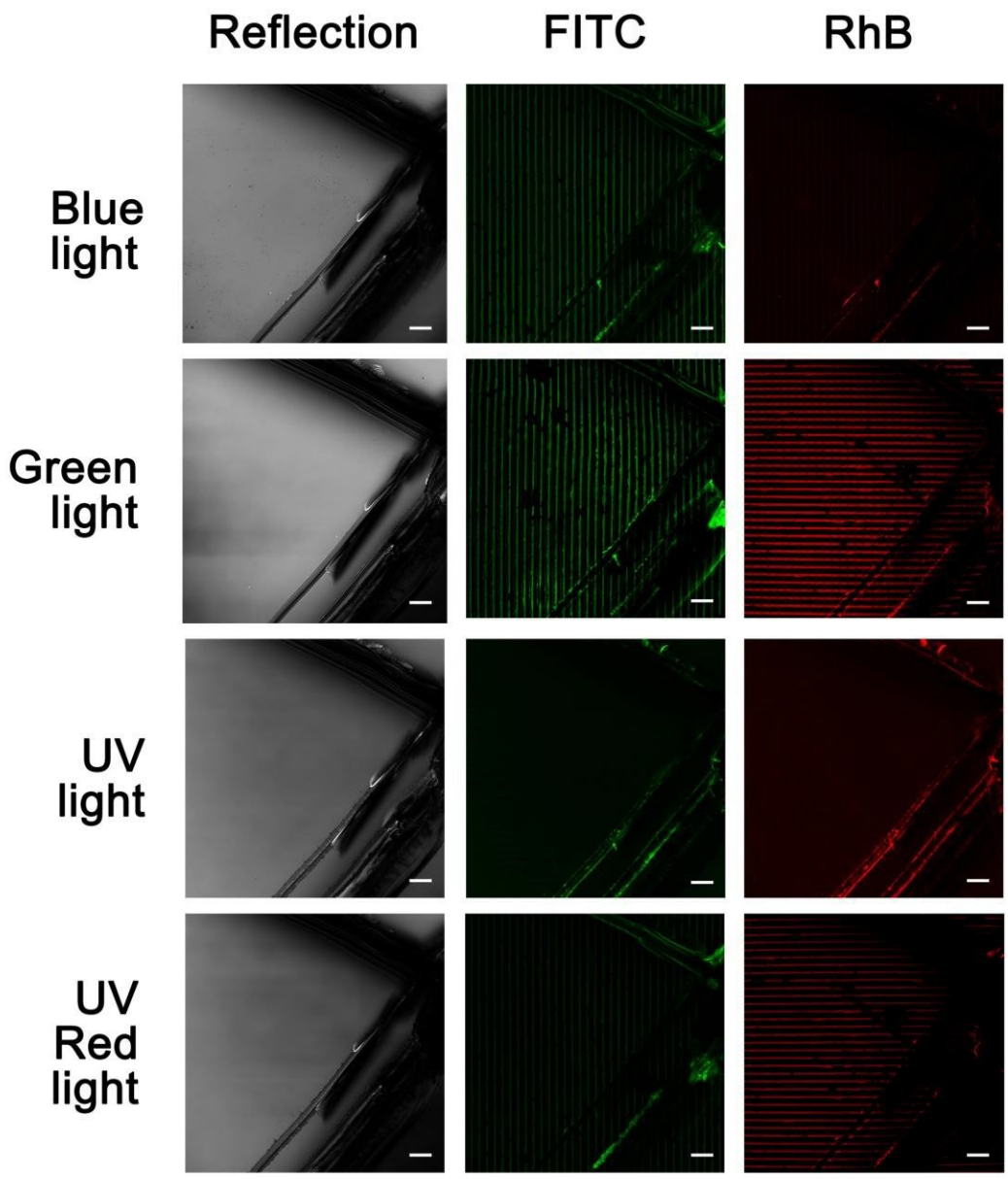


Figure S13. Confocal microscopic images of Glass-ipAzo/Azo after treating with UV, blue, green and red light irradiations. Scale bar: 30 μm.

11. NMR spectra of new chemicals

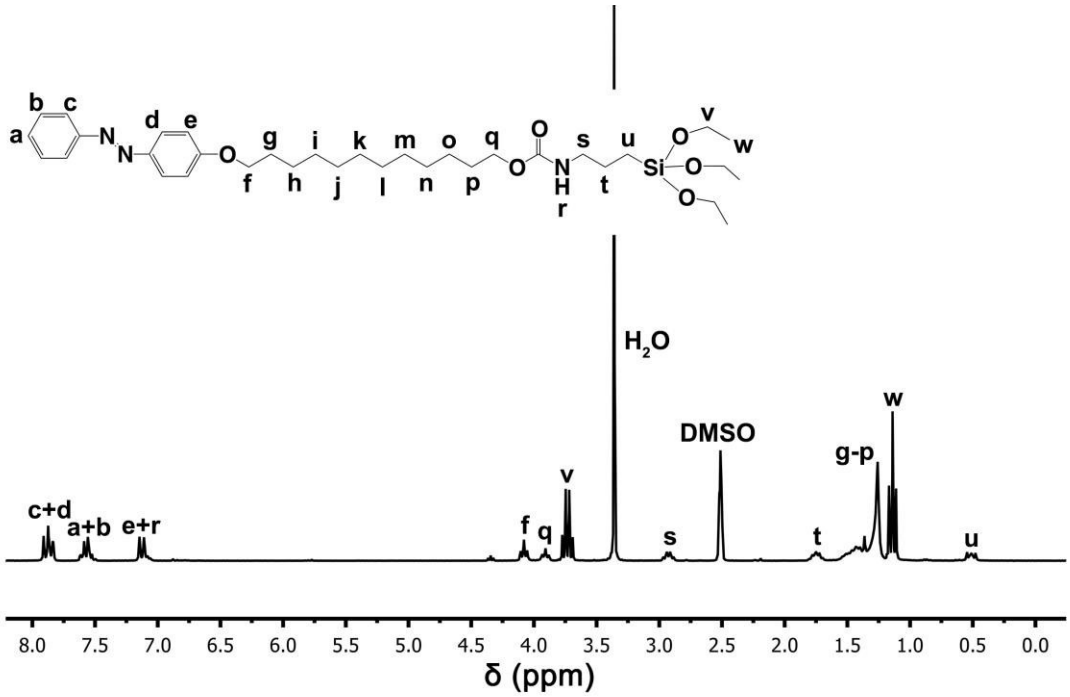


Figure S14. ^{1}H NMR spectrum of Azo-Si.

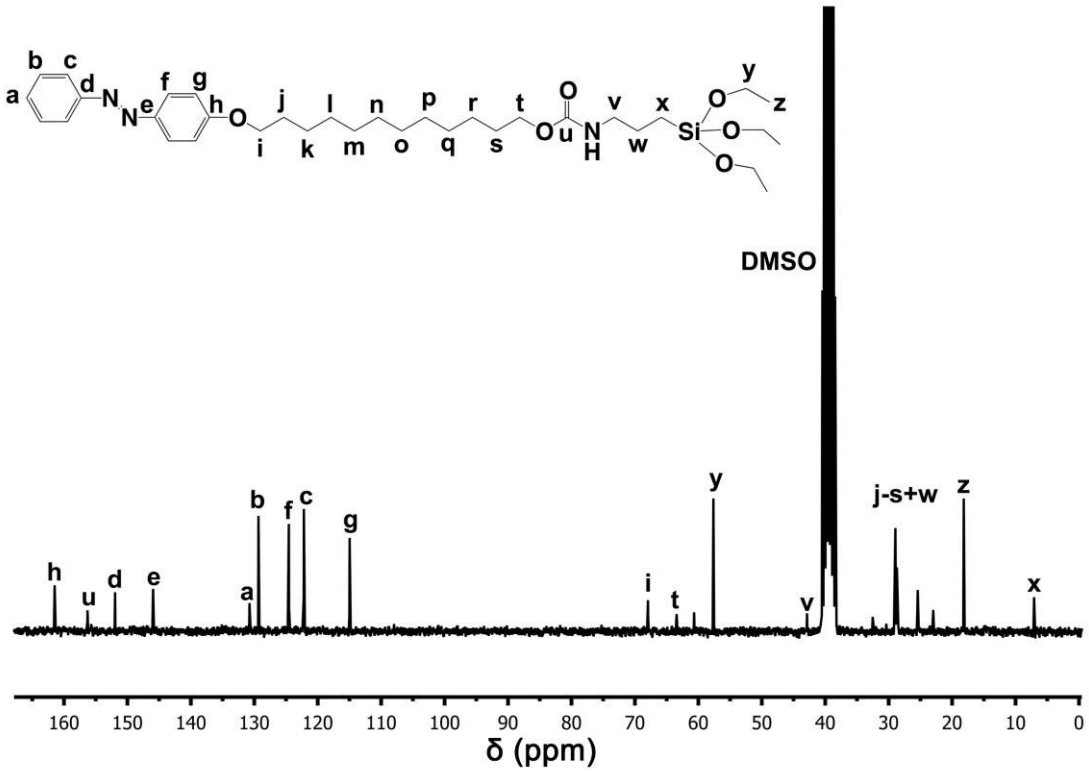


Figure S15. ^{13}C NMR spectrum of Azo-Si.

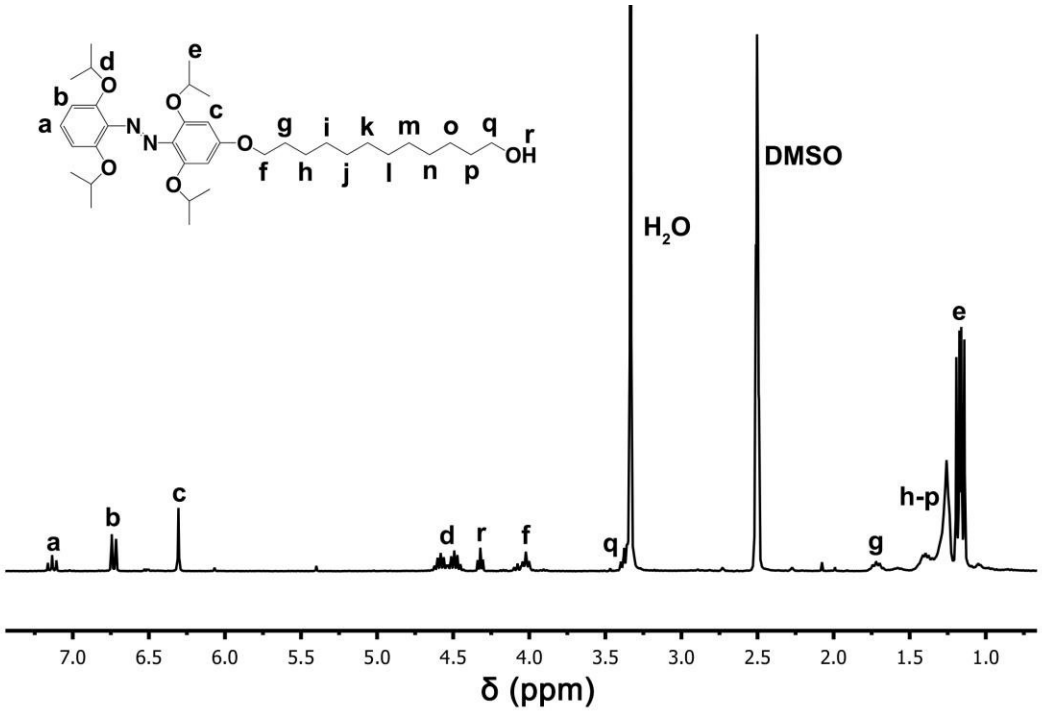


Figure S16. ^{1}H NMR spectrum of ipAzo-C_{12}.

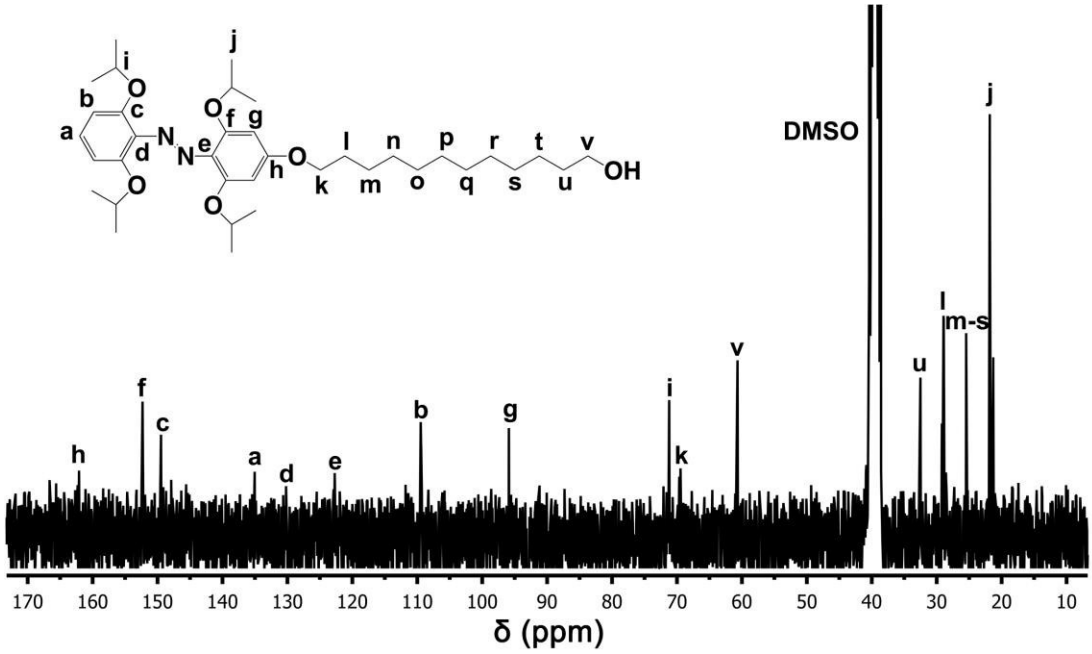


Figure S17. ^{13}C NMR spectrum of ipAzo-C_{12}.

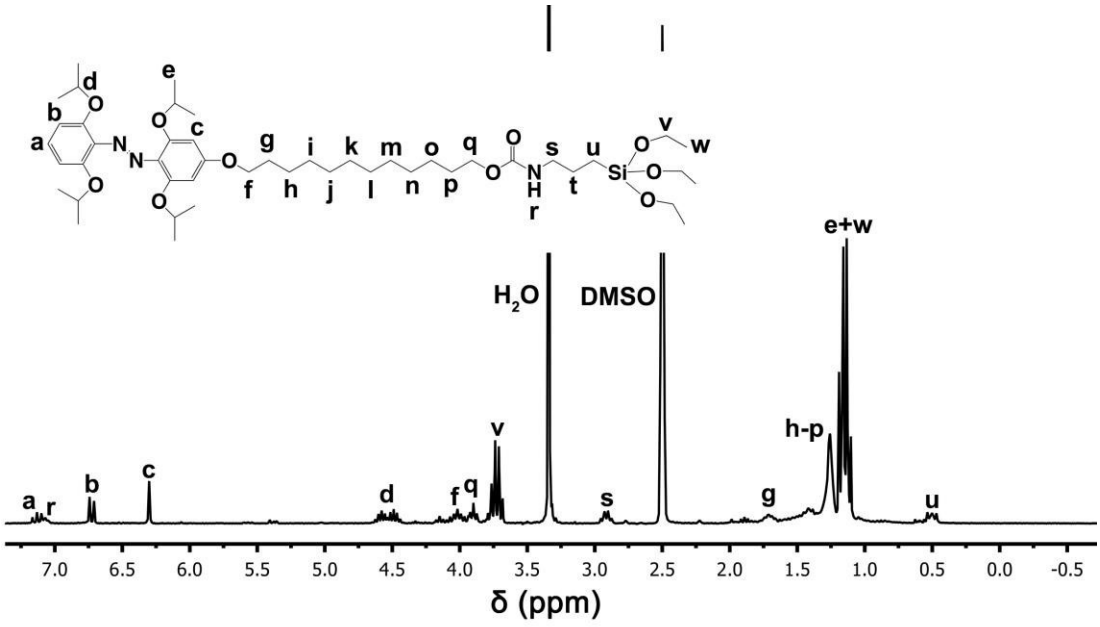


Figure S18. ^{1}H NMR spectrum of ipAzo-Si.

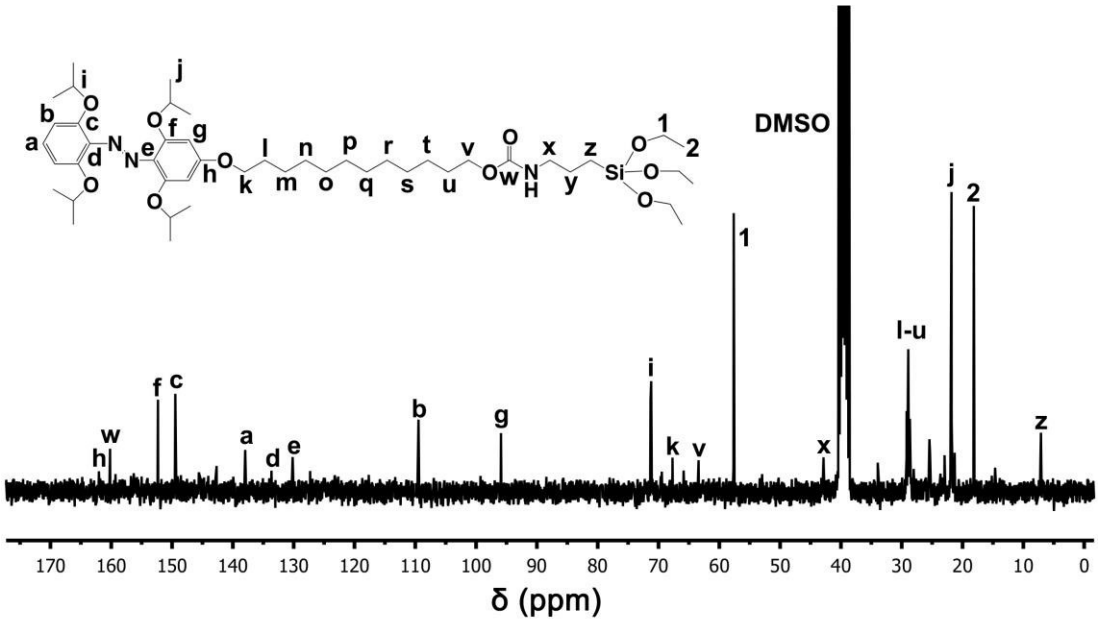


Figure S19. ^{13}C NMR spectrum of ipAzo-Si.

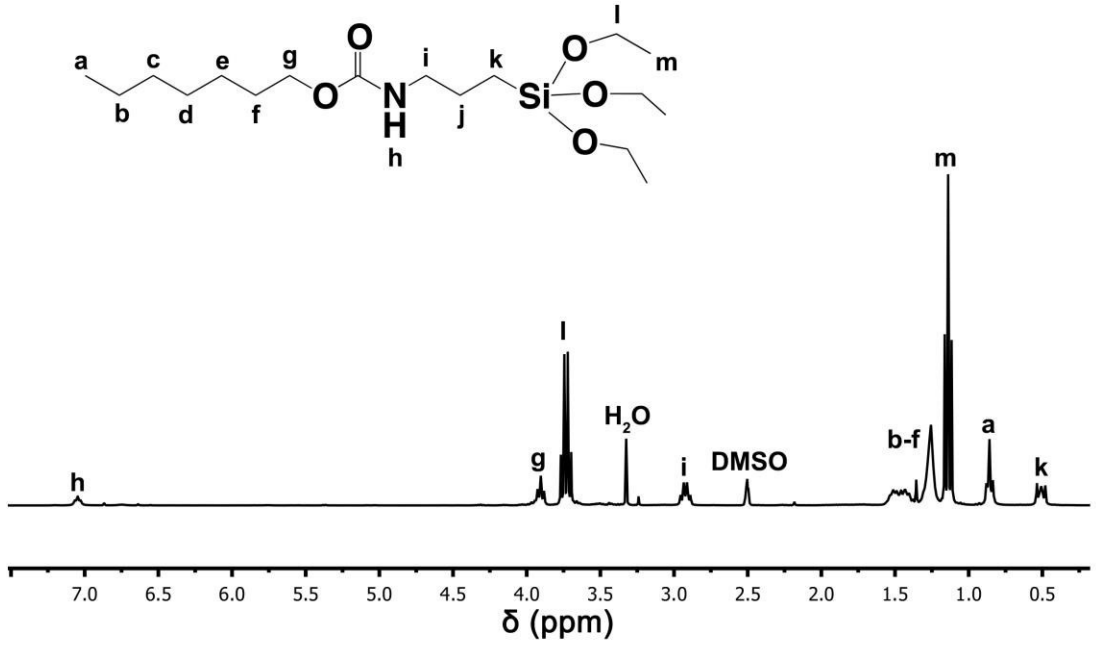


Figure S20. ^{1}H NMR spectrum of C_7-Si.

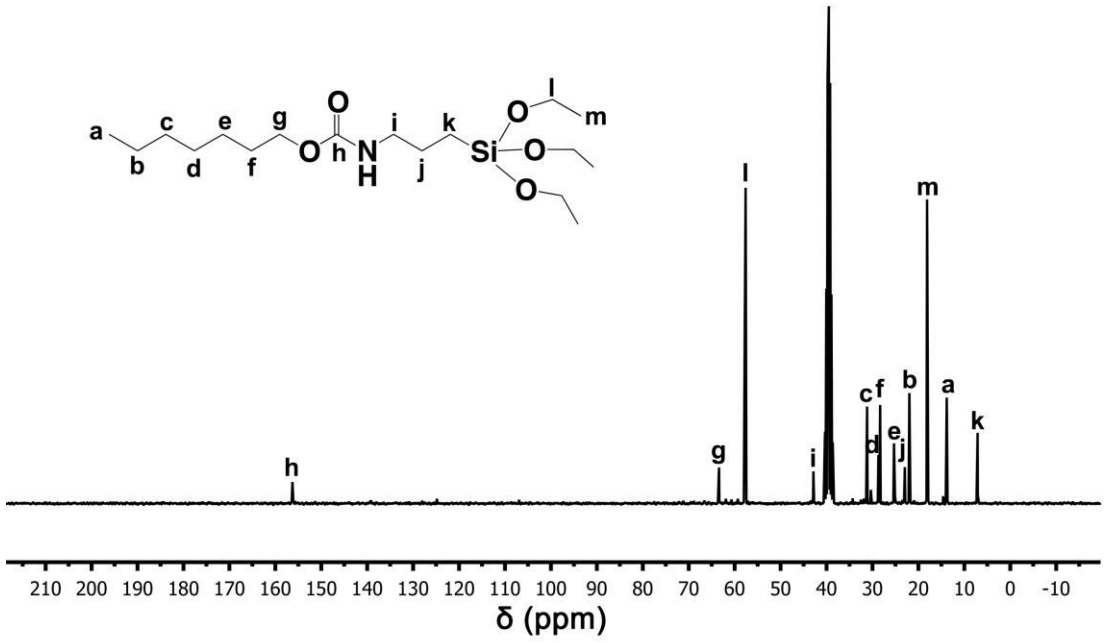


Figure S21. ^{13}C NMR spectrum of C_7-Si.

References

1. D. Wang, M. Wagner, A. K. Saydjari, J. Mueller, S. Winzen, H.-J. Butt, S. Wu, Chem. Eur. J. 2017, 23, 2628-2634.