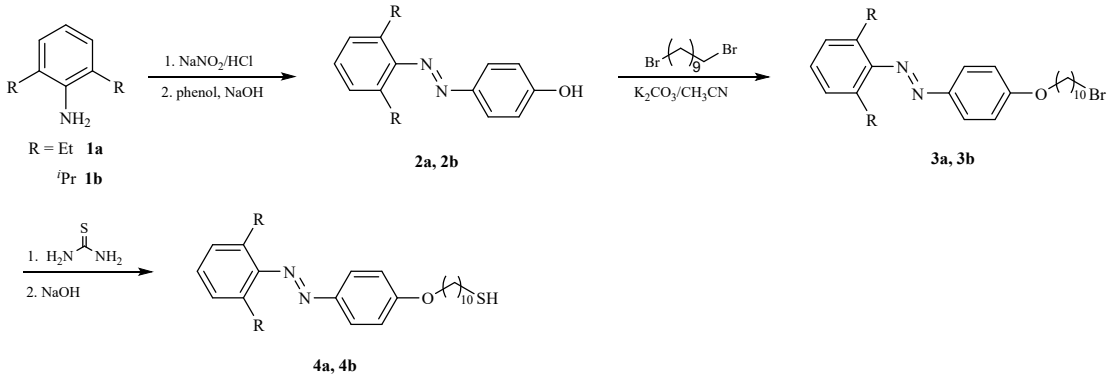
Supporting Information

Molecular Synthesis

All manipulations were carried out at room temperature under an argon atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were pre-dried, distilled and degassed prior to use. Both ^{1}H and ^{13}C spectra were acquired on a Varian Mercury Plus 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). High-Resolution Mass Spectrometry (HRMS) was recorded on Bruker micrOTOF II ESI-TOF using positive electrospray ionization (ESI). Column chromatography was performed on silica.



Scheme S1. Synthesis of azobenzene-based molecular wires **4a** and **4b**.

Synthesis of (*E*)-4-(2,6-dialkylphenyl)diazenyl)phenol (**2a** and **2b**)

A mixture of 2,6-Dialkylaniline (**1a** or **1b**, 0.033 mmol) and 3M HCl (20 ml) was stirred, and then acetone (5 mL) was added to dissolve the solid. The mixture was cooled to 0 °C with stirring for 30 minutes. Sodium nitrite (2.30 g, 0.033 mol) in 20 mL of water was added dropwise to the cooled mixture and stirred for 1 h to obtain the diazonium salt solution of 2,6-dialkyl aniline. A solution of phenols (0.033 mol) in 1M NaOH (60 mL) was prepared and cooled in an ice bath. The diazonium salt was then added slowly to the sodium phenol solution, adjusting the pH to 8-9 with an aqueous NaOH during the addition. Allow the reaction to proceed for 1 hour in the ice bath. Upon completion of the reaction, adjust the pH to neutral by adding concentrated hydrochloric acid and stirring the mixture for an additional 30 minutes at room temperature. The precipitate was then collected and washed with hexane to obtain a yellow powder. The resulting product was further purified by recrystallization using dichloromethane/hexane.

2a: yield 6.72 g, 79 %. ^{1}H NMR (400 MHz, CD_3SOCD_3): δ (ppm) 10.28 (s, 1H, OH), 7.75 (2 H, d, *J* = 8.8 Hz), 7.14-7.22 (3H, m), 6.96 (2 H, d, *J* = 8.8 Hz), 2.55 (4H, quart, *J* = 7.6 Hz), 1.05 (6H, t, *J* = 7.2).

2b: yield 8.90 g, 96 %. ^{1}H NMR (400 MHz, CD_3SOCD_3): δ (ppm) 10.29 (s, 1H, -OH), 7.75 (2 H, d, *J* = 8.8 Hz), 7.21-7.27 (3H, m), 6.96 (2 H, d, *J* = 8.8 Hz), 2.91 (2H, quin, *J* = 6.8 Hz), 1.10 (12H, d, *J* = 6.8).

Synthesis of (*E*)-1-(4-((10-bromodecyl)oxy)phenyl)-2-(2,6-dialkylphenyl)diazene (**3a** and **3b**)

A mixture of 1,10-dibromodecane (15.00 g, 0.05 mol), **2** (**2a** or **2b**, 0.01 mol), 18-crown-6 (10 mg), and K_2CO_3 (4.15 g, 0.03 mol) in 50 mL acetonitrile was refluxed with stirring for 24 h under an argon atmosphere. The reaction solution was filtered through silica gel column chromatography (CH_2Cl_2). The filtrate was evaporated under reduced pressure and purified by silica gel column chromatography (petroleum ether/dichloro-methane 3:1) to yield an orange-colored liquid compound.

3a: yield 2.45 g, 53 %. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.89 (2 H, d, *J* = 9.2 Hz), 7.12-7.21 (3H, m), 7.02 (2 H, d, *J* = 9.2 Hz), 4.05 (2H, t, *J* = 6.4 Hz), 3.42 (2H, t, *J* = 6.8 Hz), 2.64 (4H, quart, *J* = 7.6 Hz), 1.79-1.90 (m, 4H), 1.32-1.52 (m, 12H), 1.14 (6H, t, *J* = 7.6).
3b: yield 4.79 g, 96 %. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.89 (2 H, d, *J* = 9.2 Hz), 7.20-7.25 (3H, m), 7.03 (2 H, d, *J* = 9.2 Hz), 4.05 (2H, t, *J* = 6.4 Hz), 3.42 (2H, t, *J* = 6.8 Hz), 3.01 (2H, quin, *J* = 6.8 Hz), 1.79-1.90 (m, 4H), 1.32-1.52 (m, 12H), 1.17 (12H, d, *J* = 6.8).

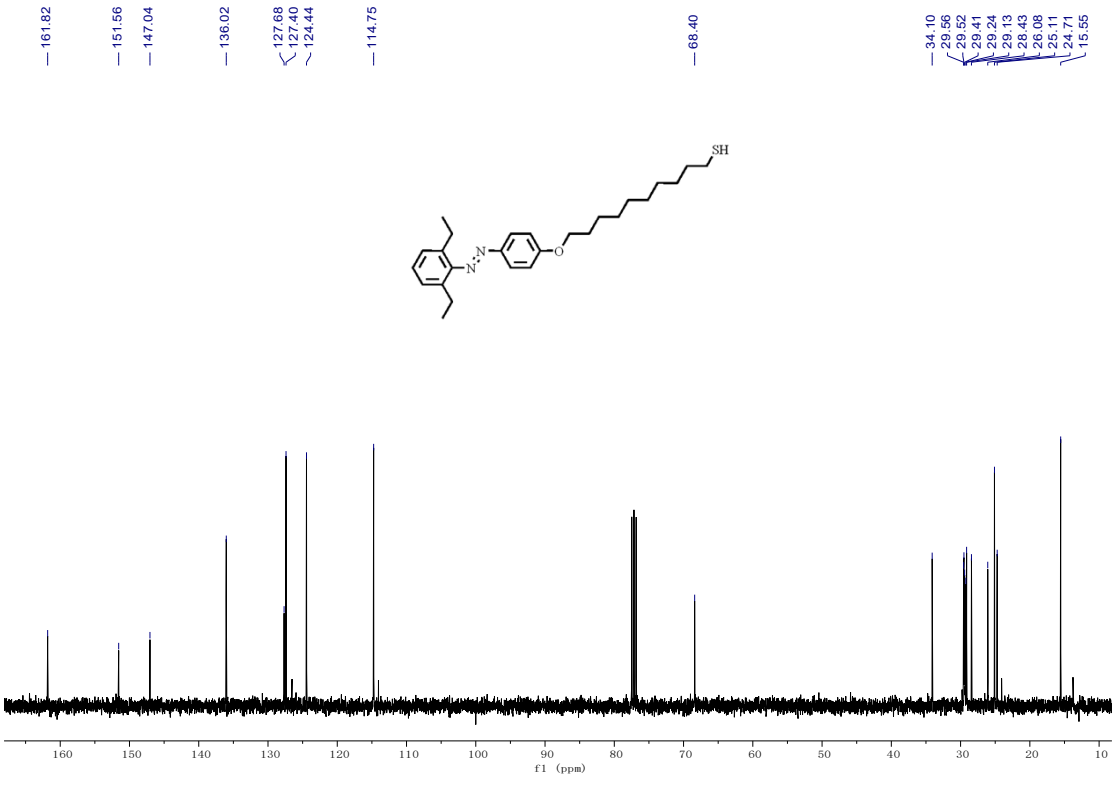
Synthesis of (*E*)-10-(4-((2,6-diethylphenyl)diazenyl)phenoxy)decanethiol (**4a** and **4b**)

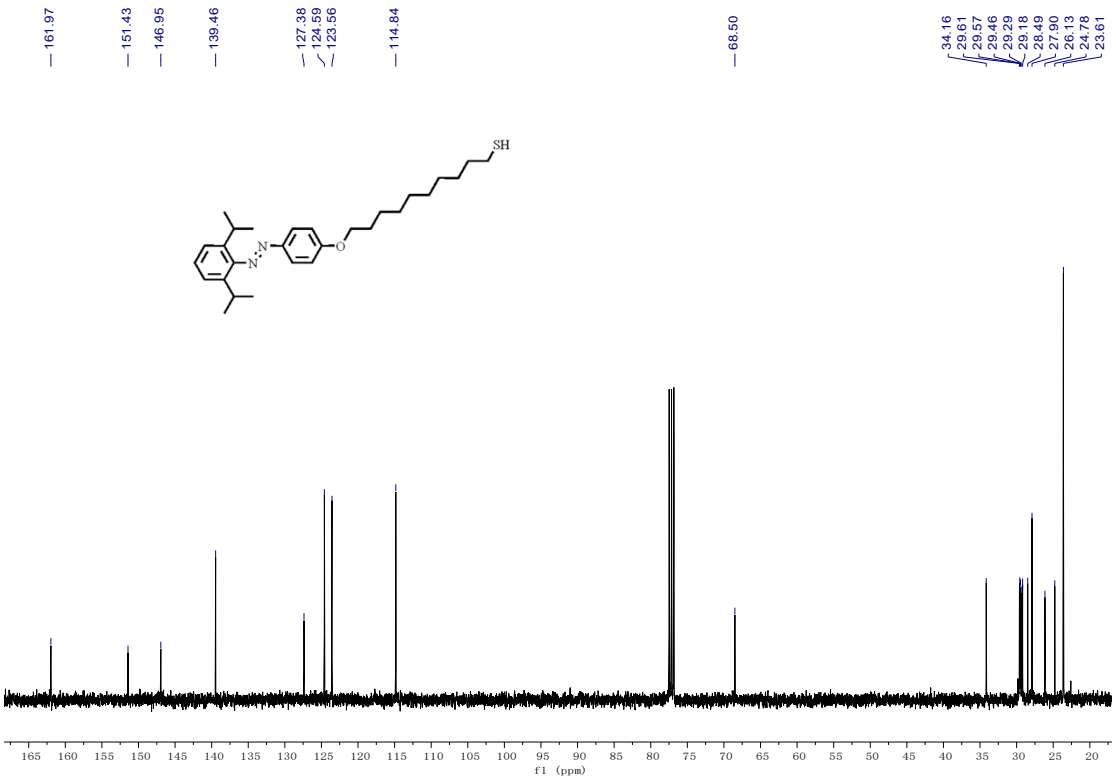
A mixture of **3** (**3a** or **3b**, 1 mmol), thiourea (0.76 g, 10 mmol), and ethanol (25 ml) was refluxed overnight in an argon atmosphere. The reaction mixture was cooled to room temperature, and 1 M NaOH (10 mL) was added. The mixture was refluxed for 3 hours, cooled to room temperature, and acidified by adding dilute HCl. The organic layer was extracted with chloroform, washed with deionized water, dried over $MgSO_4$, and filtered. The solvent was removed by evaporation, and the residue was purified by silica gel column chromatography (petroleum ether/dichloro-methane 3:1) to obtain a yellow powder.

4a: yield 0.21 g, 49 %. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.89 (2 H, d, *J* = 9.2 Hz), 7.12-7.21 (3H,

m), 7.02 (2 H, d, J = 8.8 Hz), 4.05 (2H, t, J = 6.4 Hz), 2.64 (4H, quart, J = 7.6 Hz), 2.53 (2H, quart, J = 7.2 Hz),1.79-1.87 (m, 2H), 1.57-1.65 (m, 2H), 1.44-1.52 (m, 2H), 1.28-1.40 (m, 10H), 1.34 (1H, t, J = 7.6 Hz, -SH), 1.14 (6H, t, J = 7.6). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.82, 151.56, 147.04, 136.02, 127.68, 127.40, 124.44, 114.75, 68.40, 34.10, 29.56, 29.52, 29.41, 29.24, 29.13, 28.43, 26.08, 25.11, 24.71, 15.55. HRMS (ES^+): m/z calcd for $[C_{26}H_{38}N_2OS + H]^+$: 427.2778; found: 427.2774.

4b: yield 0.18 g, 40 %. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.90 (2 H, d, J = 8.8 Hz), 7.12-7.21 (3H, m), 7.03 (2 H, d, J = 8.8 Hz), 4.05 (2H, t, J = 6.4 Hz), 3.02 (2H, quin, J = 6.8 Hz), 2.53 (2H, quart, J = 7.2 Hz),1.79-1.87 (m, 2H), 1.57-1.65 (m, 4H), 1.44-1.52 (m, 2H), 1.31-1.41 (m, 10H), 1.34 (1H, t, J = 7.6 Hz, -SH), 1.17 (12H, d, J = 7.2). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.97, 151.43, 146.95, 139.46, 127.38, 124.59, 123.56, 114.84, 68.50, 34.16, 29.61, 29.57, 29.46, 29.29, 29.18, 28.49, 27.90, 26.13, 24.78, 23.61. HRMS (ES^+): m/z calcd for $[C_{28}H_{42}N_2OS + H]^+$: 455.3091; found: 455.3095. HRMS (ES^+): m/z calcd for $[C_{28}H_{42}N_2OS + K]^+$: 493.2649; found: 493.2655.





Experiment section

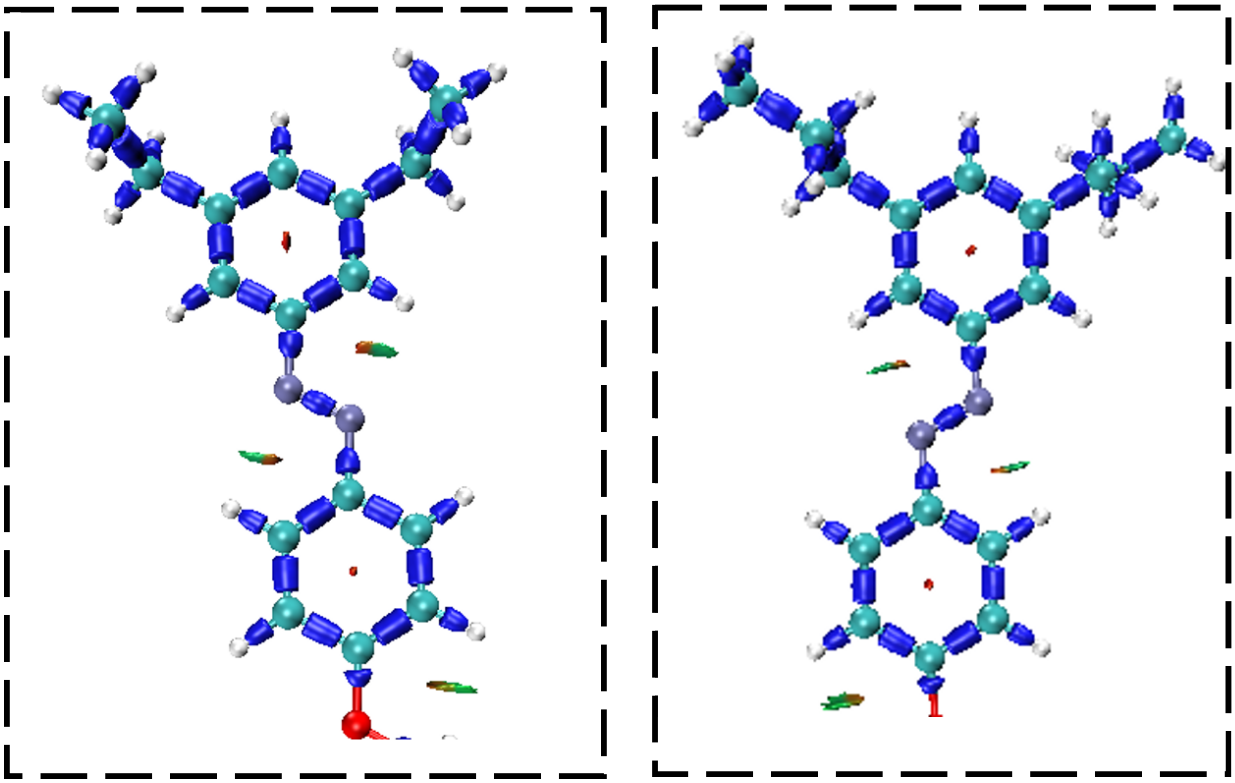


Figure S1: IRI diagram of meta-substituted Azobenzene, comparing to ortho-substituted Azobenzene, there is no obvious steric hindrance between side chain and N atom

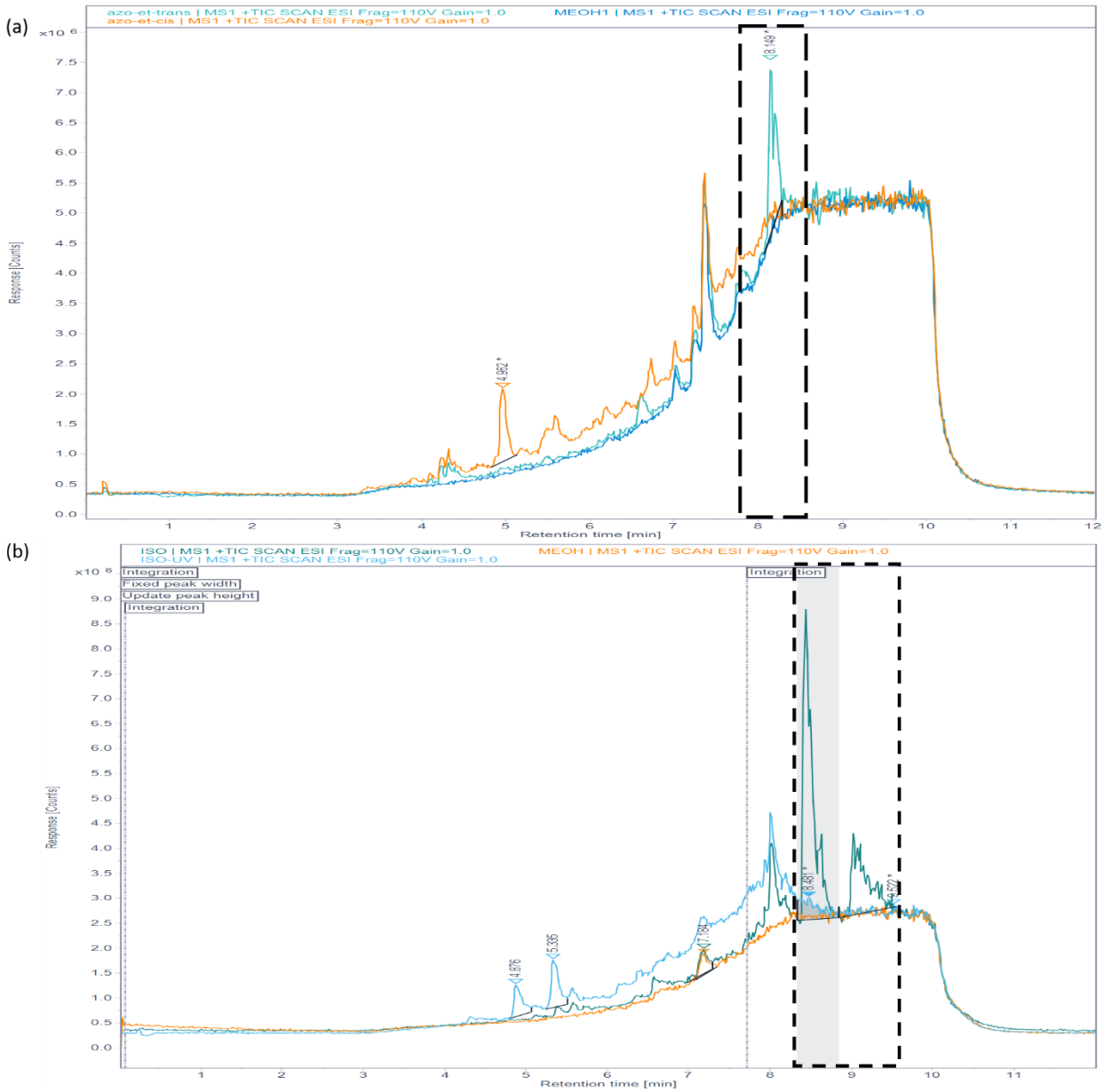


Figure S2: LCMS for ORTHO-ET(a) and ORTHO-ISO(b), the peak which is labeled by black dash box is the pristine of two molecules, after applying UV light in DCM, previous peaks disappear.

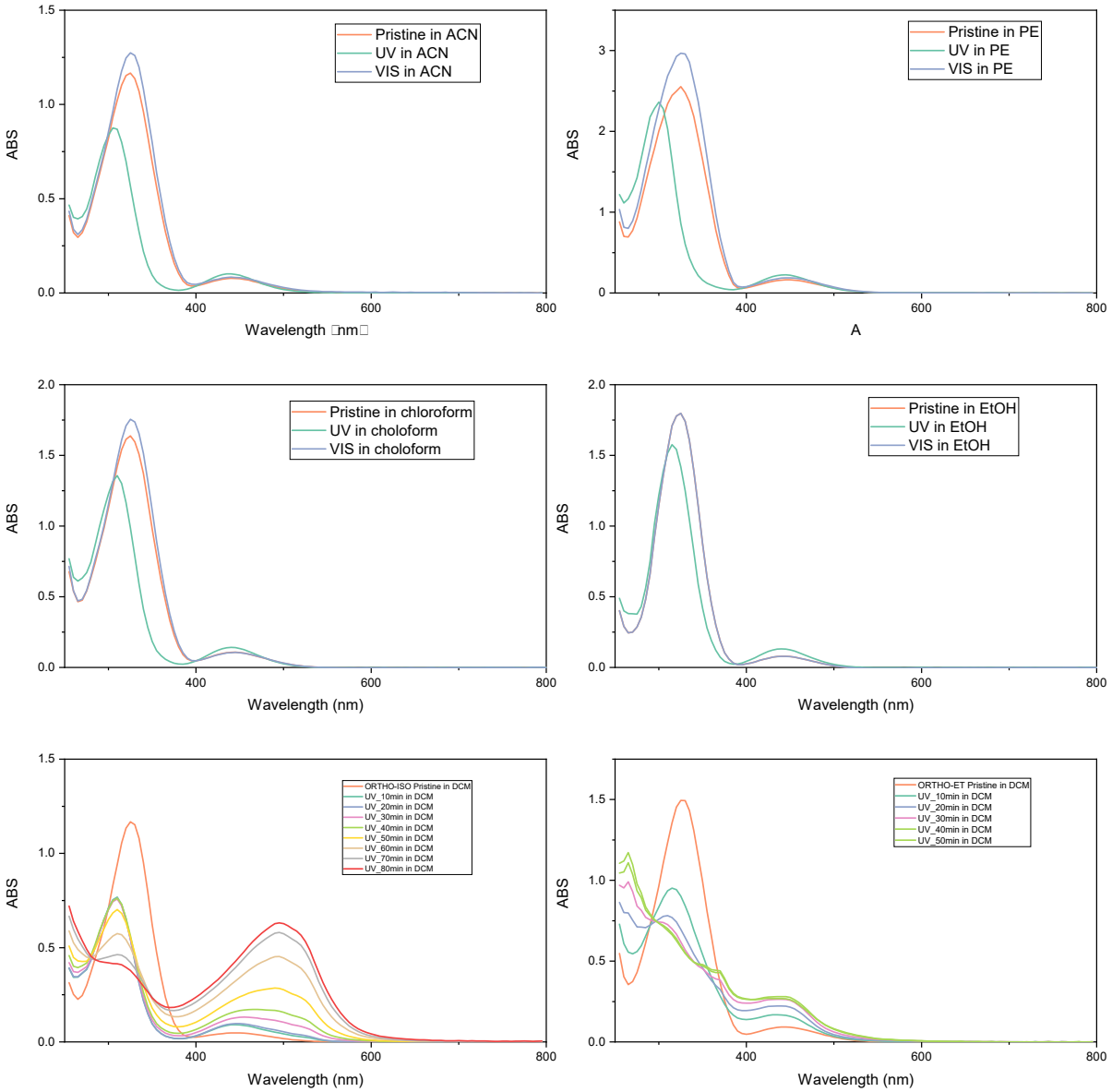


Figure S3: ORTHO-ET in different solution which has different polarity and dielectric and ORTHO-ISO and ORTHO-ET in DCM.

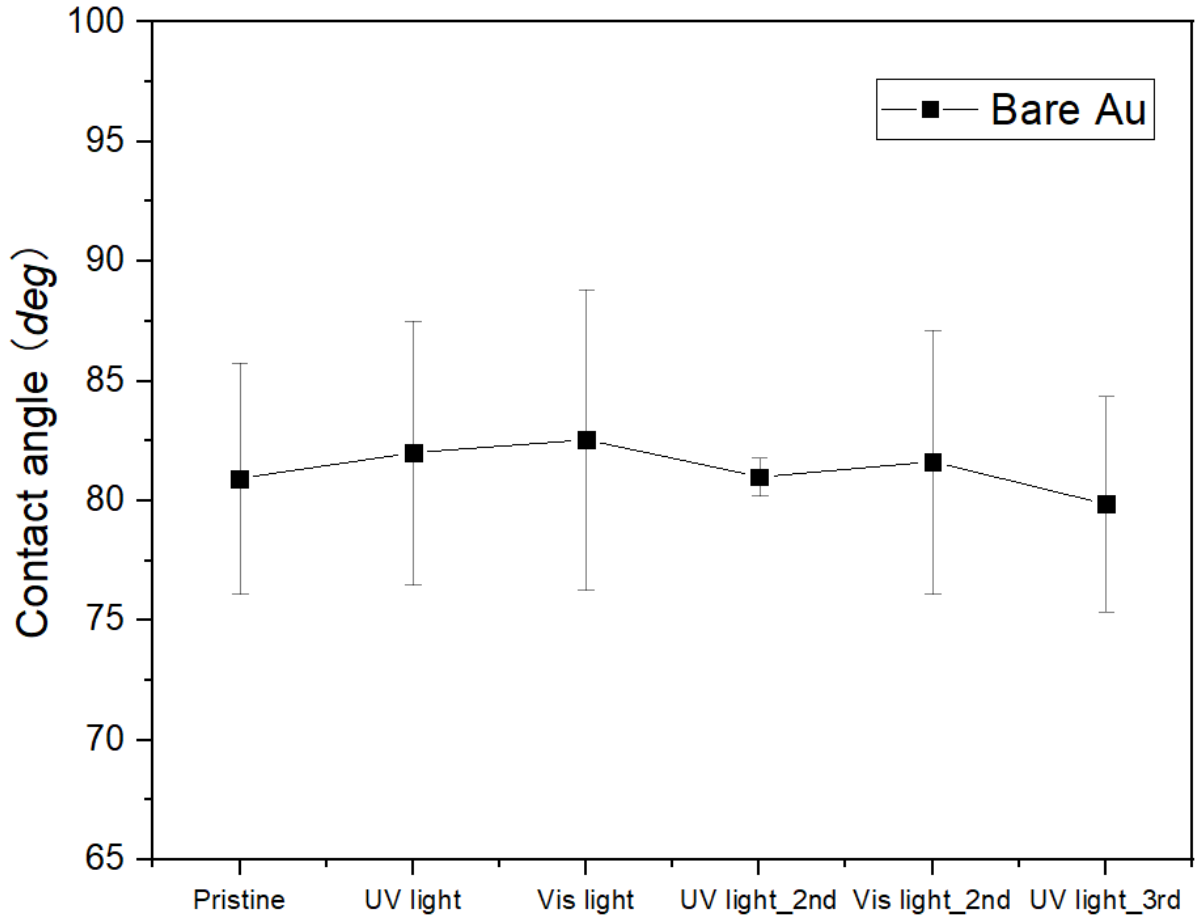


Figure S4: Bare Au has a rather stable water contact angle which guarantees the reliability of water contact angle experiment.

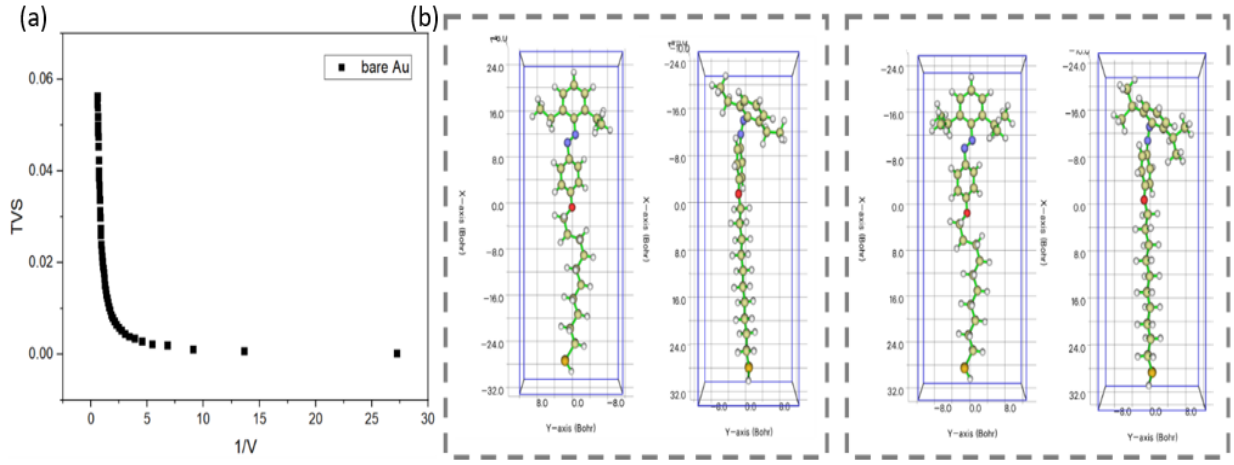


Figure S5: TVS of bare Au chip and optimized structure of ORTHO-ET and ORTHO-ISO

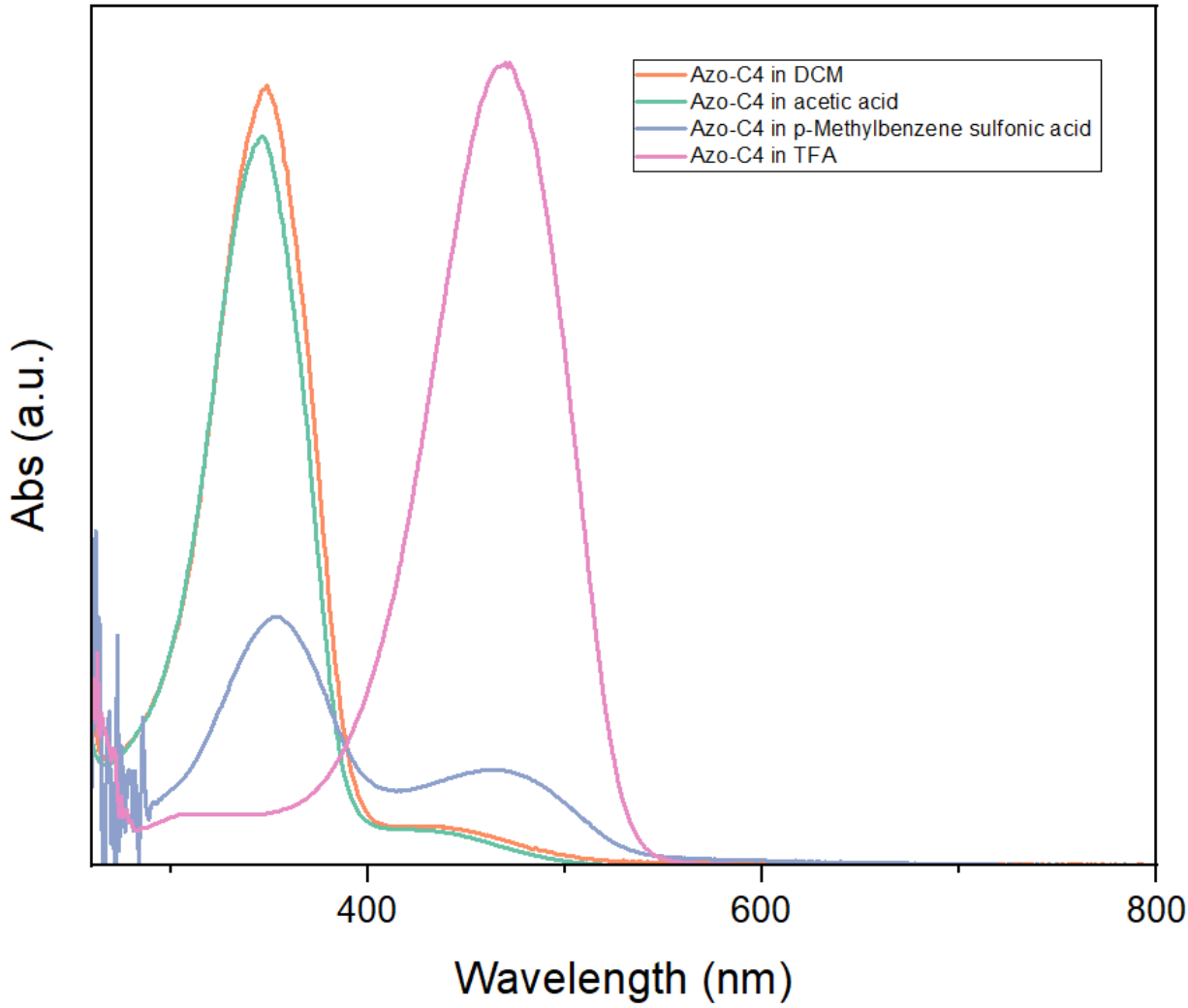


Figure S6: UV-VIS spectrum of Azo-C4 in different common organic acid, differing from TFA, acetic acid is not capable to protonate the molecule and p-Methylbenzene sulfonic acid cannot fully protonate the molecule

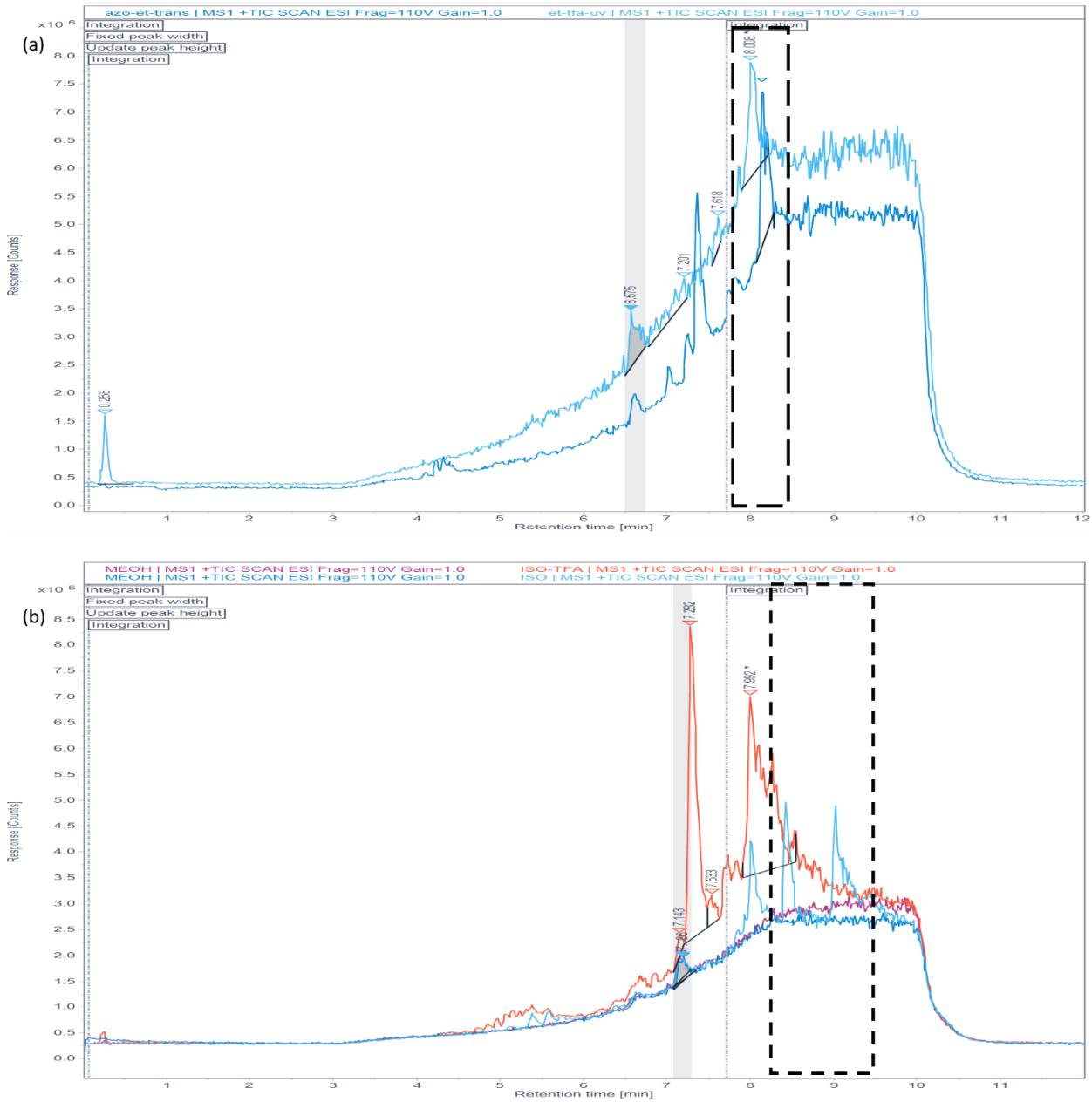


Figure S7: LCMS for ORTHO-ET(a) and ORTHO-ISO(b), the peak which is labeled by black dash box is the pristine of two molecules, after applying UV light in TFA, previous peaks disappear.

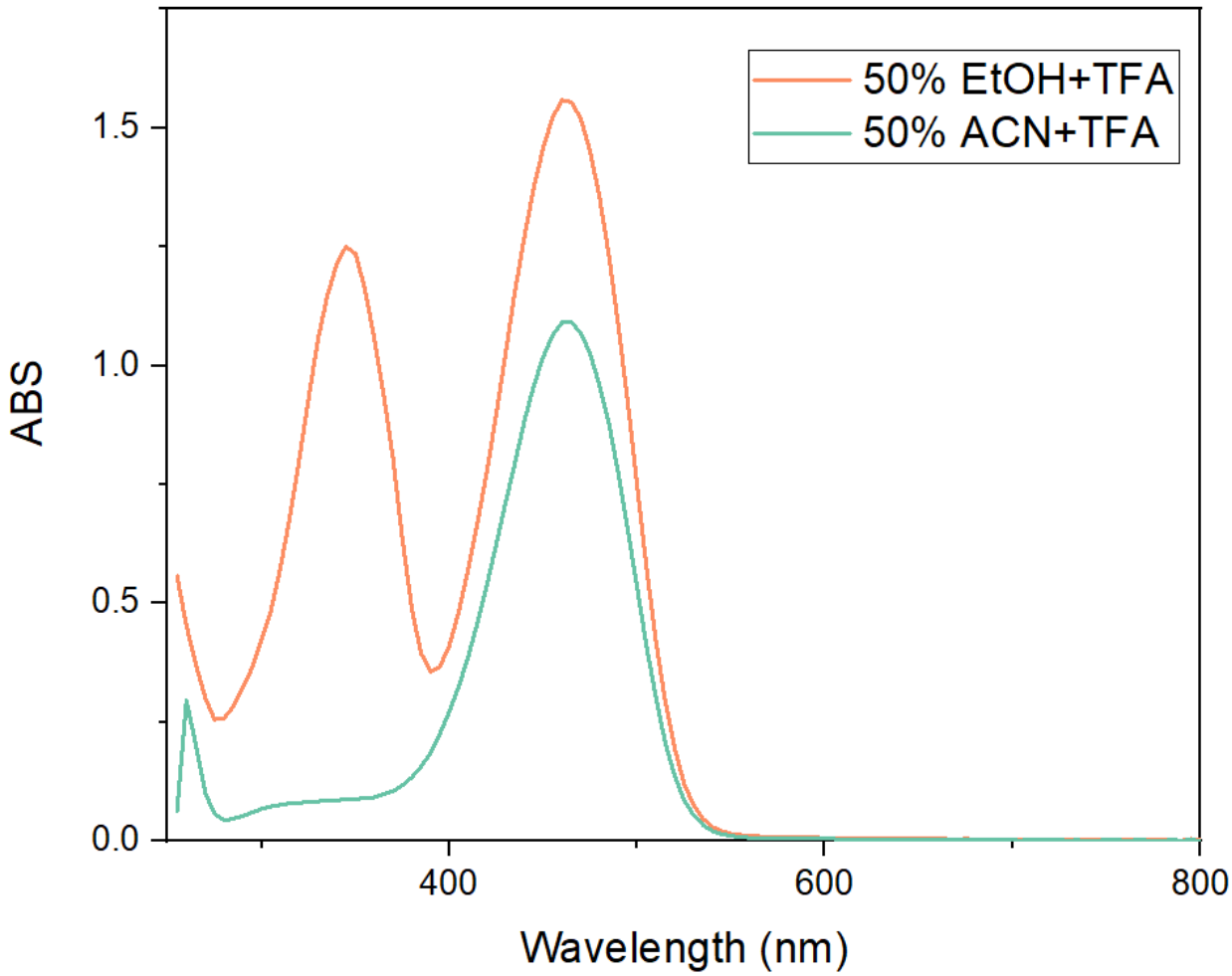


Figure S8: UV-VIS spectrum of Azo-C4 in different solution, protonated Azo_C4 will deprotonate partly in EtOH solution and can maintain in CAN.

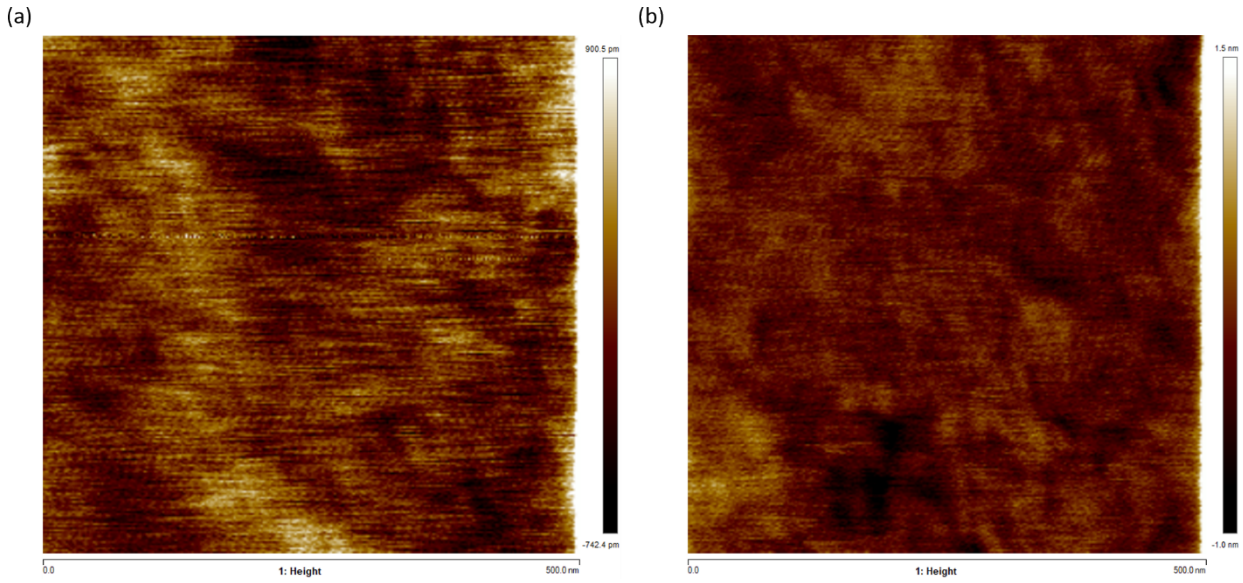


Figure S9: Topography of bare Au before (a) and after (b) 10 cycles graving

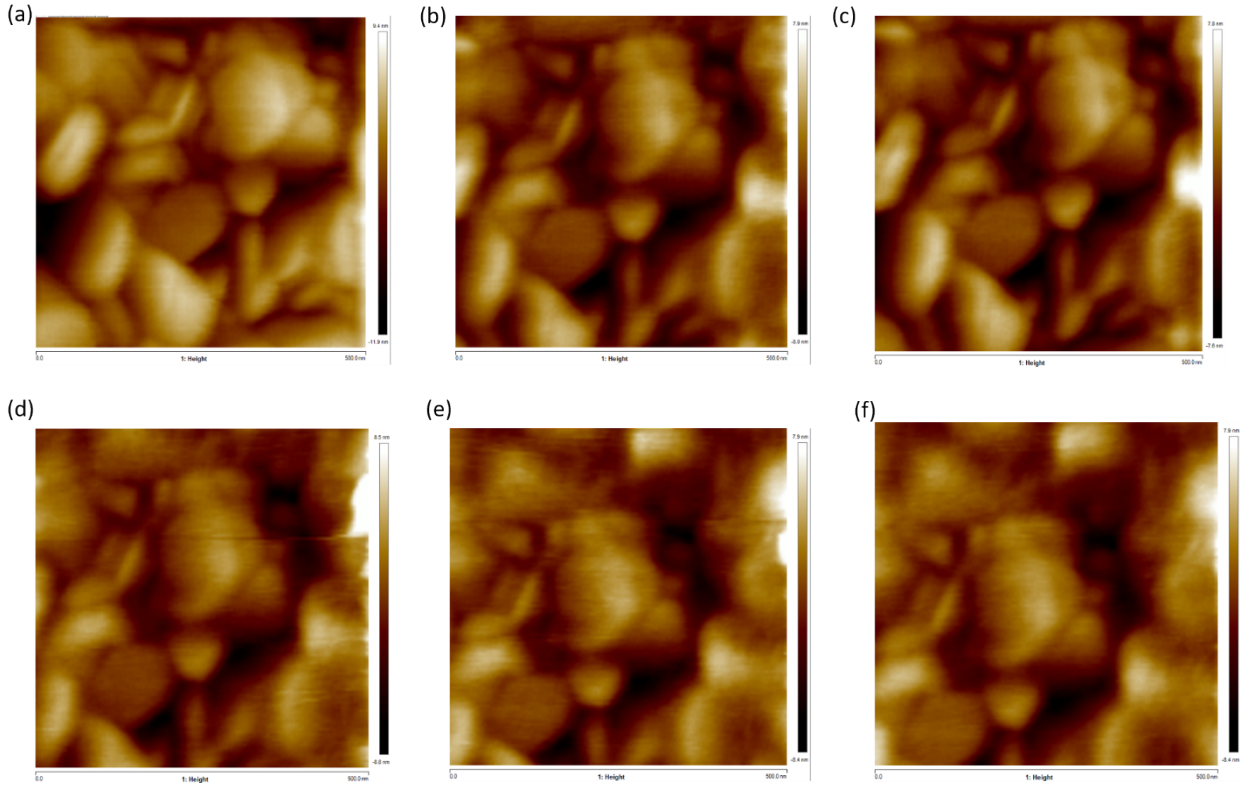


Figure S10: Au samples which is scanned by different deflection set point under contact mode. (a) 2V, (b) 1V, (c) 0.5V, (d) 0.1V, (e) 0.05V, (f) 0.01V. The resolution of Au samples does not change remarkably when applies different force on cantilever.

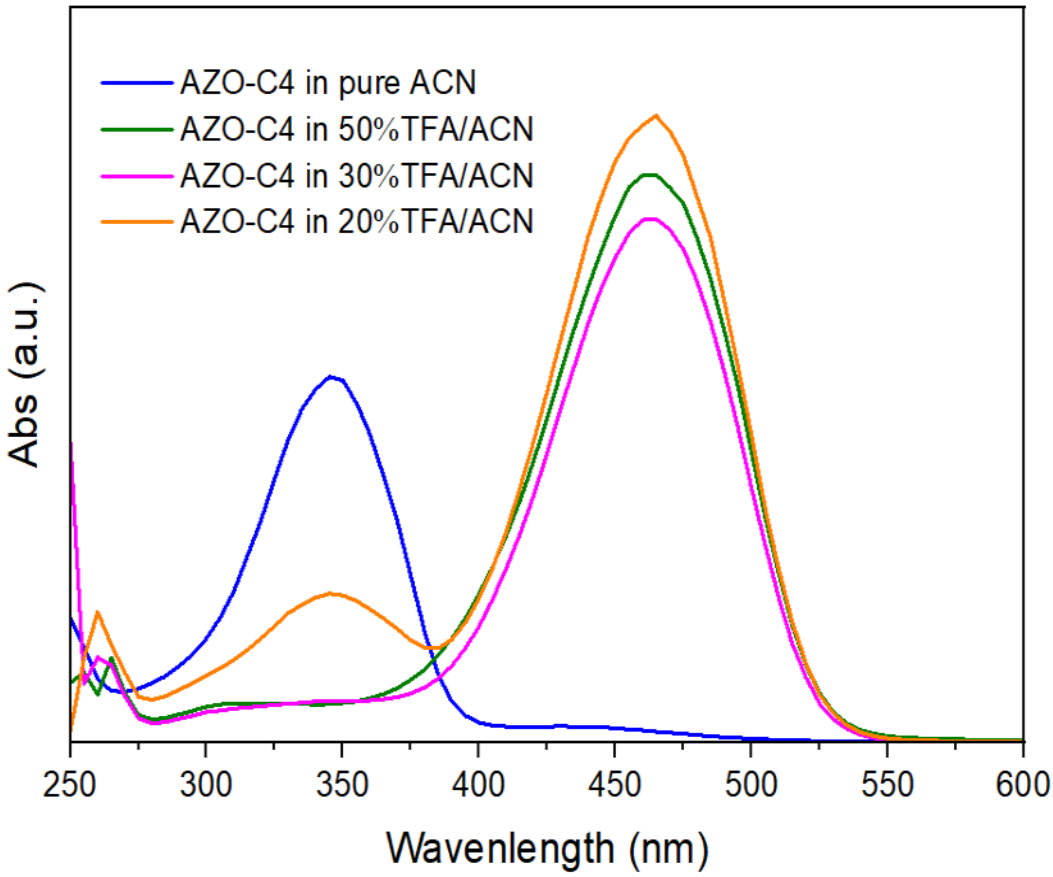


Figure S11: UV-Vis spectra for AZO-C4 under different TFA/ACN solutions, 30 % is the critical value to maintain the protonation. 50% is selected to perform the acid treatment to guarantee the fully protonation.