

## Electronic Supplementary Information (ESI)

### Direct visualization of molecular conformation changes

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## Synthesis of Et-2S

(E)-1-(4'-butoxy-3,5-diethylbiphenyl-4-yl)-2-(3-sec-butyl-4-(12-(dodecylsulfanyl)dodecyloxy) phenyl)diazene (**Et-2S**):

The precursor,

(E)-1-(4-(12-bromododecyloxy)-3-sec-butylphenyl)-2-(4'-butoxy-3,5-diethylbiphenyl-4-yl) diazene, was synthesized according to the procedure described in the literature.[ref] Sodium thiosulfate pentahydrate (1.00 g, 4.04 mmol) in 5 mL of water was added dropwise to the precursor (1.90 g, 2.69 mmol) in DMF (70 mL) solution under nitrogen atmosphere, and the mixture was stirred at 60 °C for 7 h. After being cooled to room temperature, the solvent was removed to obtain Bunte salt. A Bunte salt solution in DMF (40 mL) was slowly added to a mixture solution of dodecanethiol (0.60 g, 2.96 mmol), methanol (4 mL), and NaOH (0.13 g, 3.23 mmol) in water (2 mL), and the mixture was stirred for 5 h in the dark under nitrogen atmosphere. Ethyl acetate and water were added to the reaction mixture and the organic layer was collected. The residue was purified by silica gel chromatography (hexane:dichloromethane, v/v = 4/1). (0.41 g, Yield: 18%).

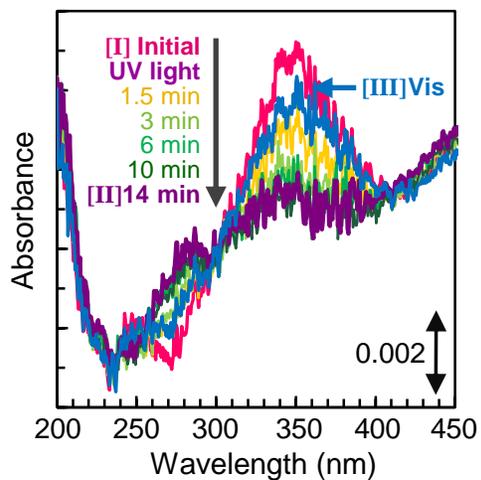
<sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>): δ 0.88 (tt, 6H, CH<sub>3</sub>), 0.97 (t, 3H, CH<sub>3</sub>), 1.2-1.9 (m, 55H, CH<sub>2</sub> and CH<sub>3</sub>), 2.70 (m, 8H, ArCH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>SSCH<sub>2</sub>), 3.15 (m, 1H, ArCH), 4.04 (tt, 4H, OCH<sub>2</sub>), 6.96 (m, 3H, Ar-H), 7.32 (s, 2H, Ar-H), 7.55-7.79 (m, 4H, Ar-H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 12.20, 13.84, 14.08, 15.56, 19.24, 20.14, 22.66, 25.43, 26.15, 28.50, (-CH<sub>2</sub>-; 29.21, 29.22, 29.27, 29.31, 29.32, 29.50, 29.54, 29.57, 29.61, 29.63, 29.68), 31.34, 31.89, 33.94, 39.19, 67.77, 68.25, 110.95, 114.73, 121.17, 121.89, 125.77, 128.04, 133.40, 136.71, 136.86, 140.05, 147.01, 150.04, 158.74, 159.28. Anal. Calcd: C, 75.46% ; H, 10.01%; N, 3.26%; S, 7.46%. Found: C, 75.52%; H, 9.91%; N, 3.30%; S, 7.26%. FAB-MS (*m/z*): [M + H]<sup>+</sup> found, 860 (= M + 1), calcd for C<sub>54</sub>H<sub>86</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> = 858.61.

## Methods

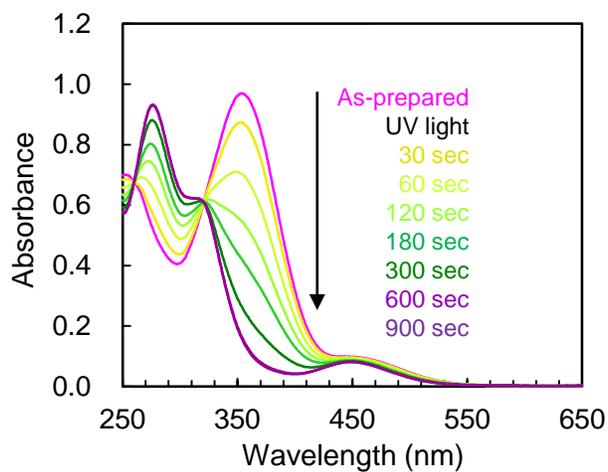
Azobenzene SAMs were formed by immersing gold substrates into 0.1 mM azobenzene solution in dichloromethane for 24 h in the dark. After immersion, the samples were sufficiently rinsed with dichloromethane, and blown dry with nitrogen gas. Azobenzene SAMs were exposed to UV light (365 nm, Supercure-204S, Tokina, combination of Toshiba color filters, UV-35+UV-D36A) to induce *trans*-to-*cis* isomerization or visible light (436 nm, combination of Toshiba color filters, Y-43+V-44) to induce *cis*-to-*trans* isomerization.

For UV-vis absorption spectroscopy measurements (Shimadzu UV3150 UV-vis-NIR spectrophotometer), polycrystalline gold films with a thickness of 20 nm were prepared on clean quartz substrates by vacuum sublimation. The UV-vis absorption spectrum of each sample was recorded in absorbance mode against air in the reference path.

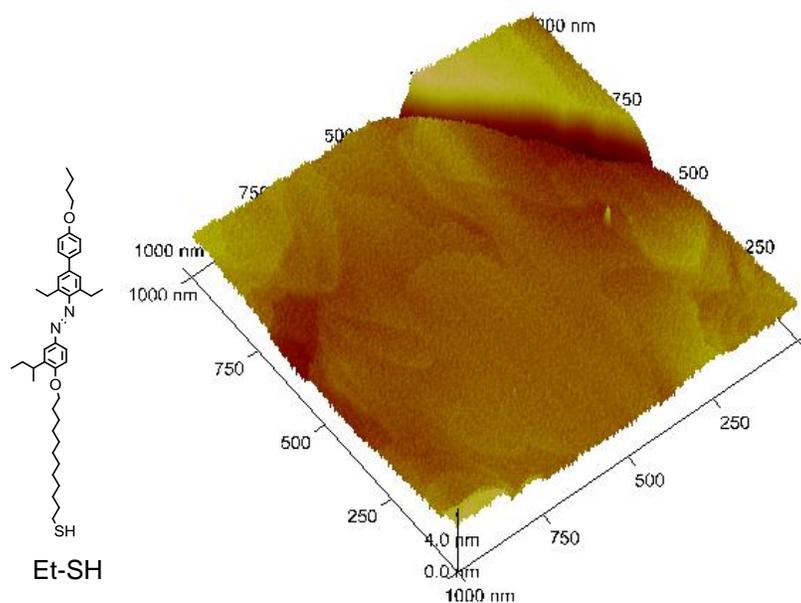
The Au(111) substrates were prepared by the vacuum deposition of gold onto freshly cleaved mica sheets with a base pressure of  $\sim 10^{-7}$  to  $10^{-8}$  Torr. After deposition, the substrates were annealed at 420 °C for 3 hours to obtain a large flat single-crystal surface. We employed tapping mode atomic force microscopy (AFM: Veeco Instruments Inc., AFM probes: NCH silicon pointprobe® tip (standard), NanoWorld, Switzerland) to characterize the topographic morphology of the samples.



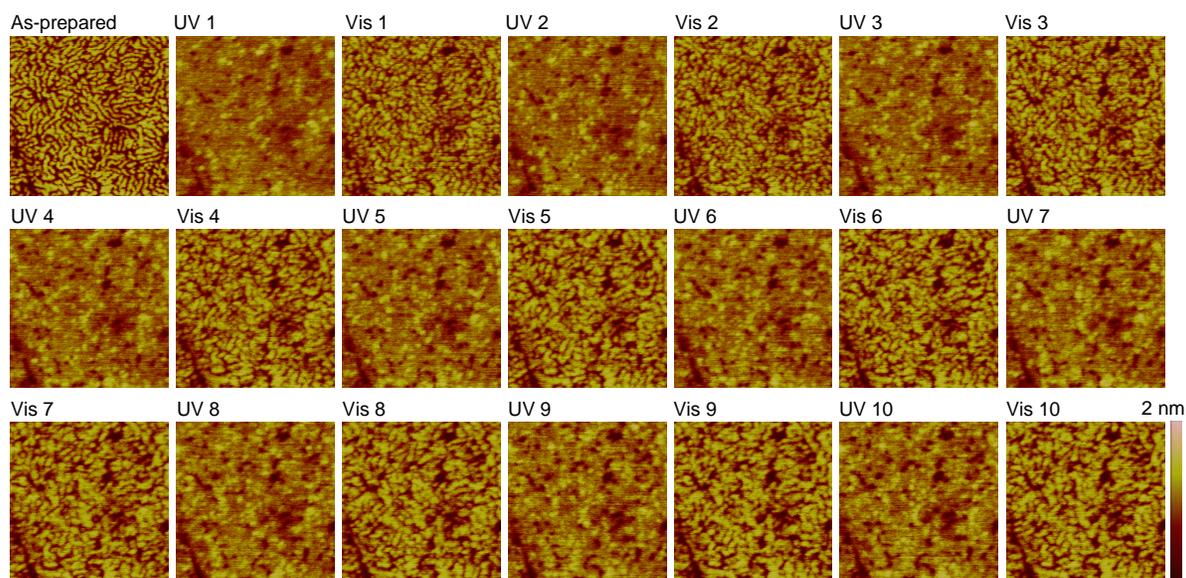
**Figure S1.** UV-vis absorption spectral changes of Et-2S SAMs on a gold film.



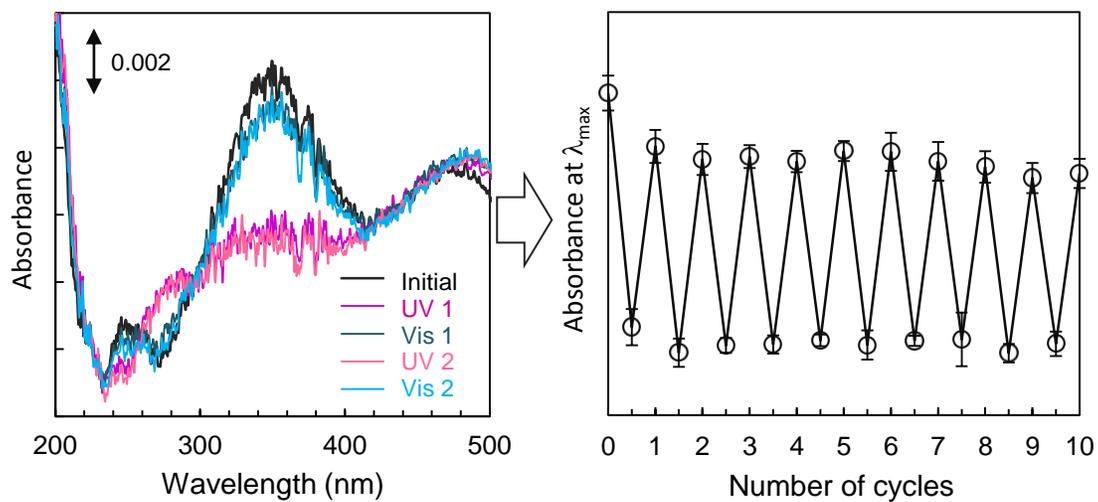
**Figure S2.** Absorption spectral changes of Et-2S in dichloromethane solution as a function of irradiation time of 365-nm light.



**Figure S3.** Three-dimensional AFM image of single-component azobenzene thiol (Et-SH) SAM on Au(111).



**Figure S4.** Continuous surface morphology changes between the worm-like structure and the smoother structure of Et-2S monolayers by continuous alternating irradiation with 365-nm and 436-nm light (at 21–22°C and 33–35% relative humidity). The dimension of the respective images is  $250 \times 250 \text{ nm}^2$ .



**Figure S5.** Reversible photoswitching of absorbance at  $\lambda_{\max}$  of Et-2S/Et-SH (1/5) mixed SAM by alternating UV and visible light irradiation.