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Light-driven molecular switches in azobenzene self-assembled monolayers: Effect of molecular structure on reversible photoisomerization and stable *cis* state

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Contents:

1. Experimental

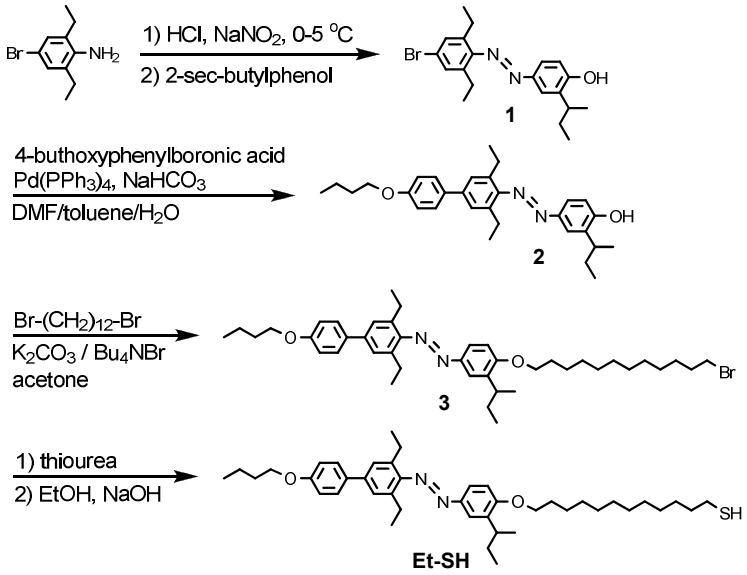
Instrumentation

Dimethylformamide (DMF) and dichloromethane of spectroscopic grade were used to dissolve the azobenzenes. After a 30-sec nitrogen purge, a screw-cap quartz cuvette containing azobenzene solution was sealed with Parafilm®. Azobenzene solutions were exposed to UV light (365 nm, Mineralight® lamp, Model UVGL-25) or visible light (436 nm, a high-pressure UV lamp, Ushio Inc., combination of Toshiba color filters, Y-43+V-44). Absorption spectra were recorded on a Shimadzu UV-3100PC UV-VIS-NIR scanning spectrophotometer. NMR spectra were obtained using JEOL JNM-EX270 (270 MHz) and JEOL JNM-ECP300 (300 MHz) spectrometers.

Monolayers preparation

Gold films with a thickness of 20 nm were prepared on quartz substrates by vacuum sublimation. The trans-azobenzene-SAMs were prepared by immersion of gold substrates in 0.1 mM azobenzene solution in dichloromethane for 24 hours in the dark. After immersion, the samples were sufficiently rinsed with dichloromethane, and blown dry with nitrogen gas.

2. Synthesis



(E)-4-((4-bromo-2,6-diethylphenyl)diazenyl)-2-sec-butylphenol (1).

A solution of $NaNO_2$ (1.27 g, 18.4 mmol) in water (15 mL) was slowly added to a solution of 4-bromo-2,6-diethylaniline (3.50 g, 15.4 mmol) and 1.6 M HCl (35 mL) at 0-5°C. A

solution of 2-sec-butylphenol (2.78 g, 18.4 mmol), NaOH (0.72 g, 18.4 mmol), and Na_2CO_3 (1.93 g, 18.4 mmol) in water (15 mL) was added to the diazonium salt solution at 0-5^oC. The mixture was stirred for 1 h at 0-5^oC, followed by the addition of water and ethyl acetate. The organic layer was separated and the solvent was removed. The residue was purified by silica gel column chromatography (hexane:ethyl acetate, v/v=10:1) to give an orange solid (4.8 g, yield: 84%).

^1H NMR (270MHz, $CDCl_3$) δ 0.89 (t, 3H, C*H*$_3$), 1.10 (t, 3H, C*H*$_3$), 1.26 (d, 3H, CHC*H*$_3$), 1.66 (m, 2H, CHC*H*$_2$CH$_3$), 2.58 (q, 4H, ArC*H*$_2$CH$_3$), 3.00 (m, 1H, ArC*H*), 5.23 (s, 1H, O*H*), 6.79 (d, J = 8.2 Hz, 1H, Ar-*H*), 7.22-7.73 (m, 5H, Ar-*H*). Anal. Calcd: C, 61.70%; H, 6.47%; N, 7.20%. Found C, 61.87%; H, 6.19%; N, 7.03.

(E)-4-((4'-butoxy-3,5-diethylbiphenyl-4-yl)diazenyl)-2-sec-butylphenol (2).

The compound (**2**) was prepared from the Suzuki coupling reaction of the precursor (**1**) in the presence of palladium(0) catalyst.[1] A catalytic amount of tetrakis(triphenylphosphine)palladium(0) was added to a solution of the precursor **1** (2.18 g, 5.6 mmol) in degassed DMF (50 mL). 4-buthoxyphenylboronic acid (2.12 g, 11.2 mmol), a solution of $NaHCO_3$ in distilled water (1N, 50 mL), and toluene (25 mL) were added to the mixture. The reaction mixture was heated under reflux for 4 h with vigorous stirring. After the mixture was cooled to room temperature, water and ethyl acetate were added. The organic layer was separated and purified by silica gel column chromatography (n-hexane:dichloromethane, v/v = 1/1) to afford as an orange solid (2.01 g, yield: 78%).

^1H NMR (300MHz, $CDCl_3$) δ 0.91 (t, 3H, C*H*$_3$), 1.00 (t, 3H, C*H*$_3$), 1.20 (t, 6H, C*H*$_3$), 1.30 (d, 3H, C*H*$_3$), 1.5-1.8 (m, 6H, C*H*$_2$), 2.75 (q, 4H, ArC*H*$_2$CH$_3$), 3.03 (m, 1H, ArC*H*), 4.02 (t, 2H,OC*H*$_2$), 5.37 (s, 1H, O*H*), 6.85 (d, J = 8.5 Hz, 1H, Ar-*H*), 6.97 (d, J = 8.5 Hz, 2H, Ar-*H*), 7.33 (s, 2H, Ar-*H*), 7.55-7.80 (m, 4H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 12.1, 13.8, 15.5, 19.2, 20.2, 25.4, 29.6, 31.3, 34.0, 67.8, 114.7, 115.7, 120.9, 122.7, 125.8, 128.1, 133.4, 134.1, 136.8, 140.1, 147.5, 149.9, 156.0, 158.7. Anal. Calcd: C, 78.56%; H, 8.35%; N, 6.11%. Found C, 78.36%; H, 8.10%; N, 5.98%.

(E)-1-(4-(12-bromododecyloxy)-3-sec-butylphenyl)-2-(4'-butoxy-3,5-diethylbiphenyl-4-yl) diazene (3).

3 was prepared by reacting **2** (3.00 g, 6.5 mmol) with 1,12-dibromododecane (6.44 g, 19.6 mmol) in acetone 60 mL in the presence of K_2CO_3 (2.71 g, 19.6 mmol) and a catalytic amount of tetrabutylammonium bromide. The reaction mixture was stirred at 60 ^oC for 7 h and then cooled to room temperature, followed by the addition of water and ethyl acetate. The organic layer was collected and the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane:dichloromethane, v/v = 3/1). (3.84 g, Yield: 83%).

^1H NMR (300MHz, $CDCl_3$) δ 0.90 (t, 3H, C*H*$_3$), 0.99 (t, 3H, C*H*$_3$), 1.2-1.9 (m, 35H, C*H*$_2$ and C*H*$_3$), 2.72 (q, 4H, ArC*H*$_2$CH$_3$), 3.09 (m, 1H, ArC*H*), 3.39 (t, 2H, C*H*$_2$Br), 4.02 (tt,

4H,OCH_2), 6.96 (m, 3H, Ar-*H*), 7.32 (s, 2H, Ar-*H*), 7.54-7.79 (m, 4H, Ar-*H*). Anal. Calcd: C, 71.47%; H, 8.71%; N, 3.98%. Found C, 71.85%; H, 8.57%; N, 3.94%.

(E)-12-(4-((4'-butoxy-3,5-diethylbiphenyl-4-yl)diazenyl)-2-sec-butylphenoxy)-dodecane-1-thiol (**Et-SH**).

3 (0.65 g, 0.92 mmol) were dissolved in dehydrated ethanol (40 mL), acetone (5 mL) and dichloromethane (5 mL). Thiourea (0.092 g, 1.20 mmol) was added to the mixture solution, and the reaction mixture was stirred at 85 ^{o}C for 8 h in the dark under nitrogen atmosphere. After being cooled to room temperature, the solvent was evaporated and the reaction residue was washed with n-hexane three times to give the isothiouronium salt. The salt was dissolved in dehydrated ethanol (40 mL), and a solution of NaOH (0.044 g, 1.10 mmol) in water (4.0 ml) was added into the reaction mixture at 85 ^{o}C for 4 h under nitrogen atmosphere. After adding sulfuric acid for neutralization of the reaction mixture, the solvent was removed and ethyl acetate and water was poured into it. The organic layer was washed with water and dried over $MgSO_4$. The solvent was removed by using a rotary evaporator, and the residue was purified by silica gel chromatography (hexane:dichloromethane, v/v = 3/1). (0.52 g, Yield: 86%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H, CH_3), 1.01 (t, 3H, CH_3), 1.2-1.9 (m, 35H, CH_2 and CH_3), 2.54 (q, 2H, CH_2SH), 2.79 (q, 4H, ArCH_2CH$_3$), 3.21 (m, 1H, ArC*H*), 4.05 (tt, 4H, OCH_2), 6.98 (m, 3H, Ar-*H*), 7.38 (s, 2H, Ar-*H*), 7.60-7.86 (m, 4H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 12.2, 13.8, 15.6, 19.2, 20.1, 24.6, 25.4, 26.1, 28.4, (-CH_2-; 29.05, 29.26, 29.29, 29.50, 29.53, 29.55, 29.68), 31.3, 33.9, 34.0, 67.8, 68.2, 111.0, 114.7, 121.2, 121.9, 125.8, 128.1, 133.4, 136.7, 136.9, 140.1, 147.0, 150.1, 158.7, 159.3. Anal. Calcd: C, 76.55%; H, 9.41%; N, 4.25%; S, 4.87%. Found C, 76.58%; H, 9.47%; N, 4.28%; S, 4.65%. FAB-MS (*m*/*z*): $[M + H]^+$ found, 660 (= M + 1), calcd for $C_{42}H_{62}N_2O_2S$ = 659.02.

Me-SH was synthesized using the same procedure of **Et-SH**.

(E)-12-(4-((4'-butoxy-2-methylbiphenyl-4-yl)diazenyl)-2-sec-butylphenoxy)dodecane-1-thiol (**Me-SH**).

Yield: 41%. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, 3H, CH_3), 0.97 (t, 3H, CH_3), 1.2-1.8 (m, 29H, CH_2 and CH_3), 2.35 (s, 3H, ArCH_3), 2.49 (q, 2H, CH_2SH), 3.14 (m, 1H, ArC*H*), 4.01 (tt, 4H, OCH_2), 6.89-6.94 (m, 3H, Ar-*H*), 7.22-7.32 (m, 3H, Ar-*H*), 7.69-7.99 (m, 4H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 12.2, 13.9, 19.3, 20.3, 20.7, 24,6, 26.1, 28.3, (-CH_2-; 29.05, 29.27, 29.30, 29.50, 29.54, 29.76), 31.4, 33.9, 34.0, 67.7, 68.2, 111.0, 114.1, 120.0, 121.8, 122.0, 124.2, 130.2, 130.6, 133.5, 136.3, 136.7, 143.6, 146.8, 151.8, 158.4, 159.2. Anal. Calcd: C, 75.93%; H, 9.15%; N, 4.54%; S, 5.20% S. Found: C, 75.68%; H, 8.85%; N, 4.57%; S, 5.07%. FAB-MS (*m*/*z*): $[M + H]^+$ found, 617 (= M + 1), calcd for $C_{39}H_{59}N_2O_2S$ = 616.41.

Reference

1. N. Miyaura and A. Suzuki, *Chem. Rev*. 1995, **95**, 2457.

Table S1. UV-vis absorption properties and half-life times of **Et-SH** and **Me-SH** in dichloromethane solution.

Cpd	π–π* (nm)/ε (L mol^{-1} cm^{-1})	n–π* (nm)/ε (L mol^{-1} cm^{-1})	$t_{1/2}$ (h)[c]
Et-SH	354 (26,000)	449 (2,600[a], 2,100[b])	380
Me-SH	368 (36,000)	447 (3,400[b])	13

[a] as-prepared (*trans*-rich state). [b] after UV light irradiation (*cis*-rich state). [c] half-life of the *cis* form at 293 K.

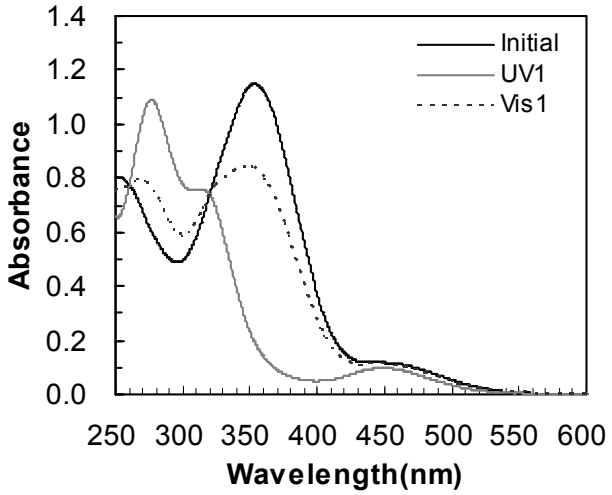


Fig. S1 Absorption spectral changes of **Et-SH** in dichloromethane solution after UV and subsequent visible light irradiation.

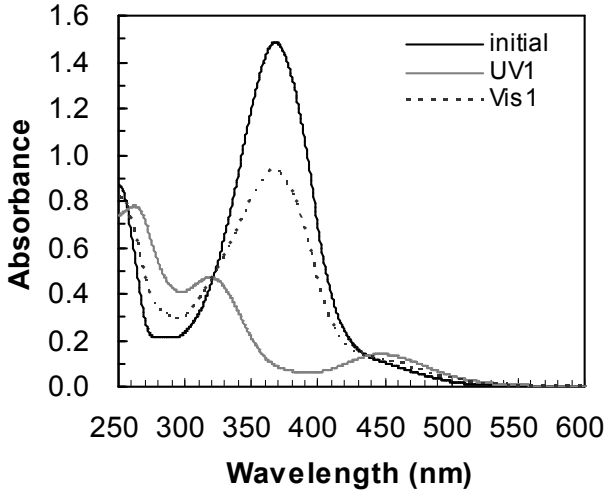


Fig. S2 Absorption spectral changes of **Me-SH** in dichloromethane solution after UV and subsequent visible light irradiation.

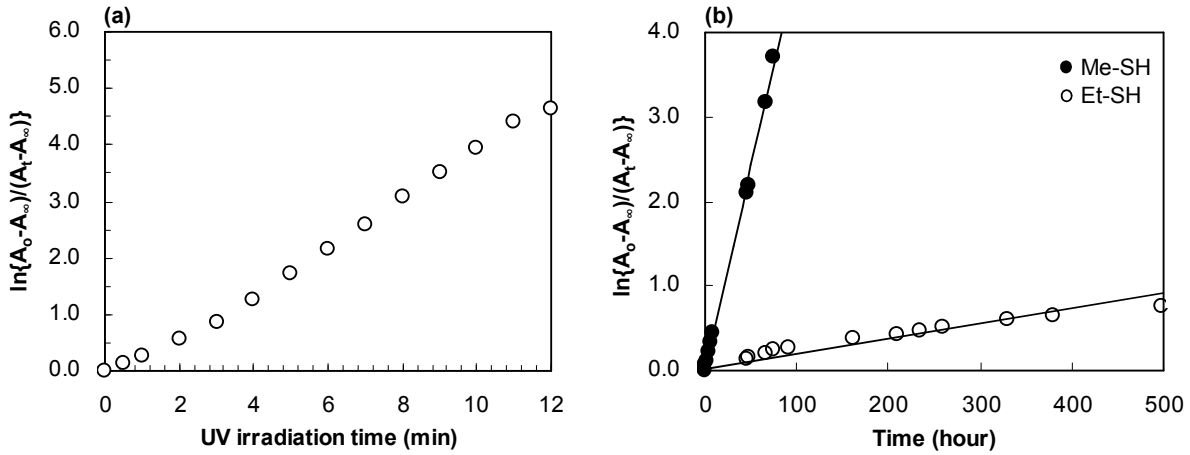


Fig. S3 First-order plots for (a) *trans*-to-*cis* photoisomerization of **Et-SH** and (b) thermal *cis*-to-*trans* isomerization of **Et-SH** and **Me-SH** in dichloromethane at 20^{o}C.

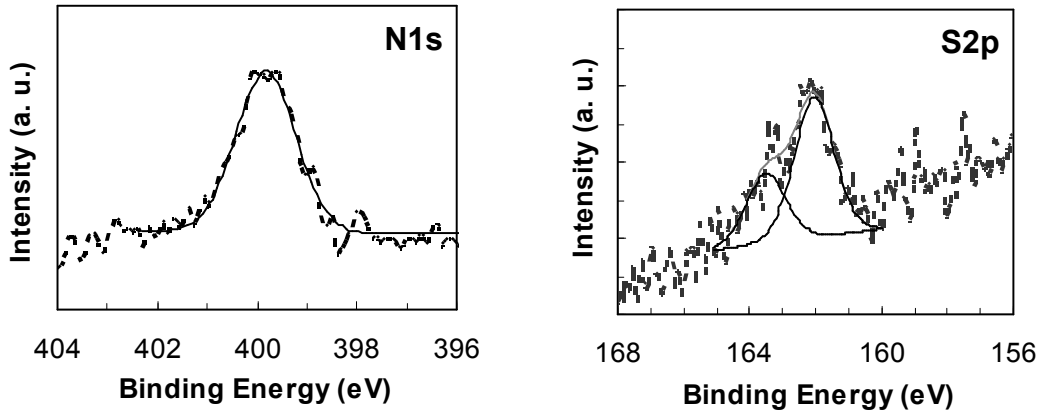


Fig. S4 N1s and S2p XPS spectra (dotted lines) of **Et-SH** SAMs, together with the corresponding fits (solid line).

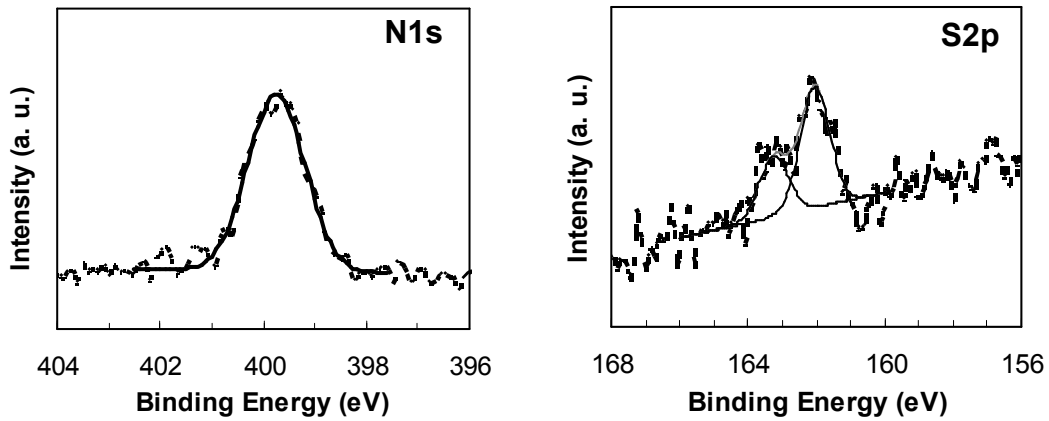


Fig. S5 N1s and S2p XPS spectra (dotted lines) of **Me-SH** SAMs, together with the corresponding fits (solid line).

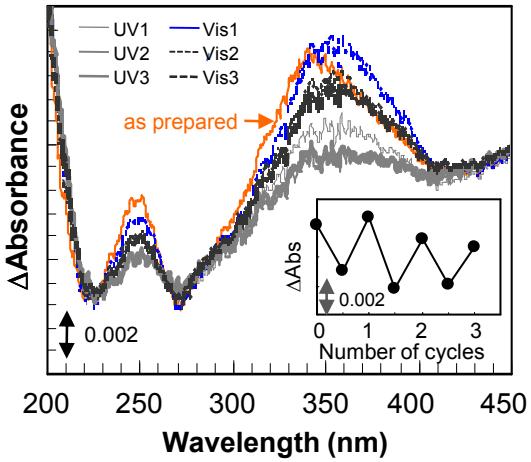


Fig. S6 UV-vis absorption spectral changes after alternating UV and visible light irradiation of **Me-SH** SAMs on a gold surface.