Supporting Information for:

A Photoswitchable Methylene–Spaced Fluorinated Aryl Azobenzene Monolayer Grafted on Silicon

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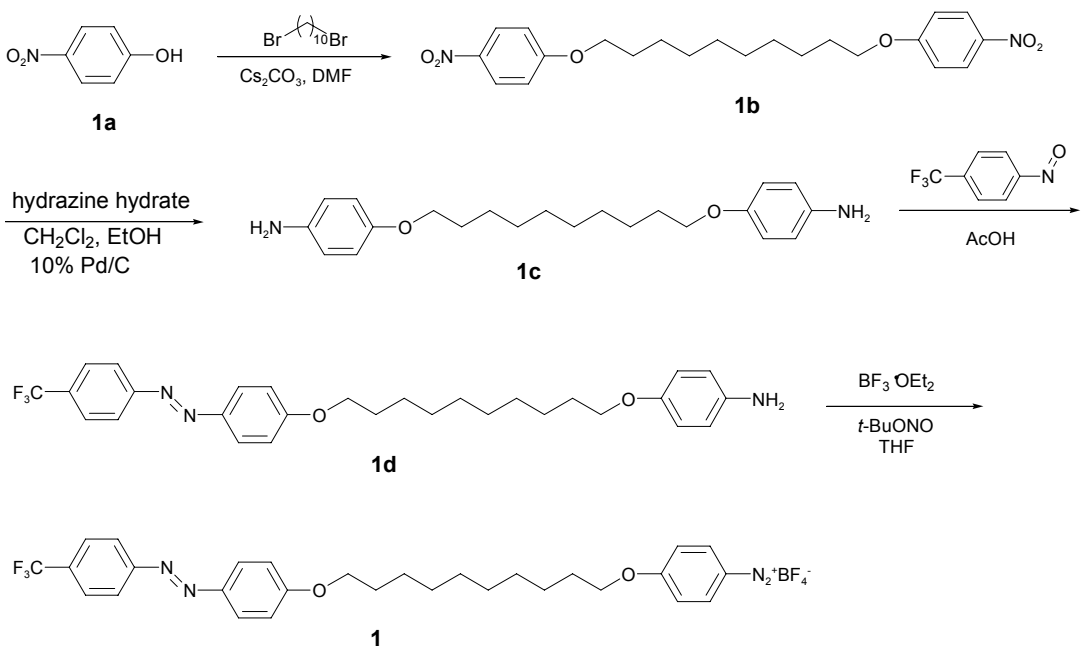
Experimental Section

Chemicals and Materials. The trifluoromethyl azobenzene diazonium salts were prepared according to literature procedures.[1] Acetonitrile (CH_3CN, 99.5+%) packed under nitrogen in a Sure Seal® container. 4-aminoazobenzne was purchased from TCI. For surface reactions, was purchased from Aldrich. Acetone, CH_3CN, chloroform, and water used for rinsing were purchased as HPLC grade and used without further purification. Ammonium fluoride (NH_4F) was purchased from Aldrich. Concentrated sulfuric acid (H_2SO_4) and 30 % hydrogen peroxide (H_2O_2) were purchased as reagent grade. Before use, all diazonium salts were stored under nitrogen in tightly capped vials.

Instruments. *Ellipsometric measurements.* Measurements of molecular layer thickness were taken with a multi-wavelength (400-900 nm laser) spectroscopic ellipsometer (Model M-2000, J. A. Woollam Co., USA) with a 75˚ incident angle. The observed error in repeated measurements of the same spot was typically 0.2 nm or less.
Contact angle measurements. Water contact angle measurements were performed using a Goniometer (Phoenix, model-300).
X-ray Photoelectron Spectroscopy (XPS) measurements. ThermoVG Scientific ESCA X-ray Photoelectron Spectrometer (Sigma probe) with an Al-Kα source at 5.0 x 10^{-9} Torr source at 100 W was used with an analytical spot size of 1.2 mm^2 and a 30° or 90° takeoff angle, with a pass energy of 20 eV.



Scheme S1. Synthesis of the methylene-spaced aryl azobenzene diazonium salt **1**.

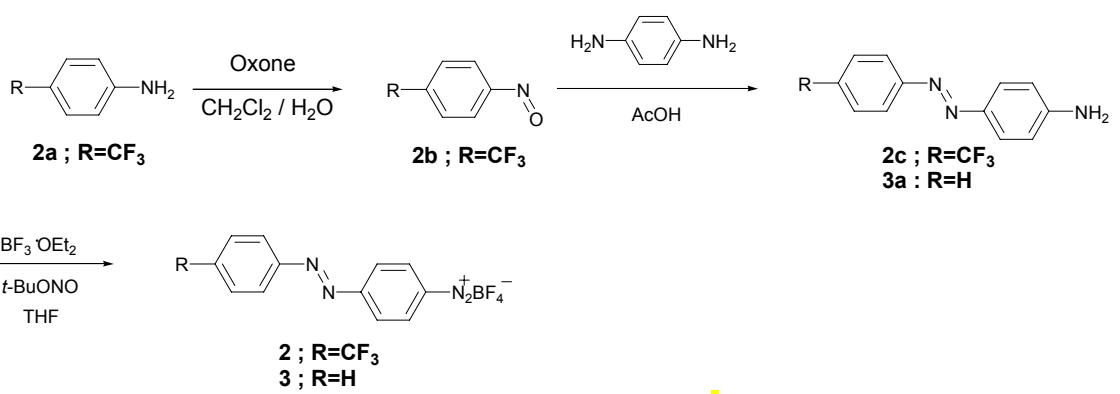
[1] (a) B. C. Yu, Y. Shiral, J. M.Tour, *Tetrahedron,* 2006, 62,10303 (b) B. Priewisch and K. J. Ruck-Braun, *Org.Chem*, 2005, **70**, 2350

1,10-*bis*(4-Nitrophenoxy)decane (1b) To a solution of 9.24 g (66.4 mmol) of 4-nitrophenol in 45 mL of DMF was added 10.0 g (33.2 mmol) of 1,10-dibromodecane and 10.0 g (33.2 mmol) of cesium carbonate. The mixture was stirred for 24 h at 50 ℃. Water was then added and the aqueous layer was separated and extracted with CH_2Cl_2 three times. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with 40% CH_2Cl_2 in hexanes gave 7.20 g (56% yield) of the dimer **1b**: FTIR (KBr) 3109, 3080, 2925, 2855, 1604, 1592, 1510, 1471, 1340, 1276, 1174, 1112, 1010, 751 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.21 (2H, d, J = 9.2 Hz) 6.95 (2H, d, J = 9.2 Hz), 4.05 (4H, t, J = 6.5 Hz), 1.82 (4H, m), 1.60-1.22 (12H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 164.2 (2C), 141.2 (2C), 125.8 (4C), 114.5 (4C), 68.8 (2C), 29.4 (6C), 25.9 (2C); CI mass spectrum, *m/z* (%): 417 ([MH^+], 14).

4,4'-(Decane-1,10-diylbis(oxy))dianiline (1c) To a solution 2.90 g (6.96 mmol) of 1,10-*bis*(4-nitrophenoxy)decane in 40 mL of a mixture of CH_2Cl_2 and EtOH (1:1) was added 4.35 mL of hydrazine hydrate and 250 mg of Pd/C (10%). The mixture was stirred for 24 h. The reaction mixture was then filtered with MeOH on Cellite(245) and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with CH_2Cl_2 gave 2.0 g (47% yield) of the dianiline **1c**: FTIR (KBr) 3403, 3310, 2922, 2847, 1566, 1510, 1319, 823 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.74 (4H, d, J = 8.5 Hz), 6.63 (4H, d, J = 8.5 Hz), 3.87 (4H, t, J = 6.6 Hz), 3.31 (4H, brs), 1.76-1.68 (4H, m), 1.45-1.26 (12H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 152.3 (2C), 139.7 (2C), 116.3 (4C), 115.7 (4C), 68.6 (2C), 29.4 (6C), 26.0 (2C); CI+ mass spectrum, *m/z* (%): 357 ([MH^+], 100).

(E)-4-(10-(4-((4-(Trifluoromethyl)phenyl)diazenyl)phenoxy)decyloxy)aniline (1d) To a solution 2.00 g (5.61 mmol) of the dianiline **1c** in 25 mL of AcOH was added 1.47 g (8.42 mmol) of nitrosobenzene at room temperature. The mixture was stirred for 36 h. Water was then added the aqueous layer was separated and extracted with CH_2Cl_2 three times. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with 30% ethyl acetate in hexanes gave 600 mg (31% yield) of the monoazobenzene **1d**: FTIR (KBr) 3105, 2299, 1577, 1532, 1361,1344, 1319, 1077, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (2H, d, J = 8.5 Hz), 7.93 (2H, d, J = 8.7 Hz), 7.74 (2H, d, J = 8.5 Hz), 7.00 (2H, d, J = 8.9 Hz), 6.73 (2H, d, J = 8.7 Hz), 6.62 (2H, d, J = 8.7 Hz), 4.04 (2H, t, J = 6.5 Hz), 3.87 (2H, t, J = 6.5Hz), 3.39 (2H, brs) 1.84-1.71 (4H, m) 1.48-1.34 (12H, m); ^{13}C NMR 75.5 MHz, $CDCl_3$) δ 162.4, 154.7, 152.3, 146.7 (2C), 139.8 (2C), 131.4 (q, $^2J_{CF}$ = 32.5 Hz), 125.4 (q, $^1J_{CF}$ = 271 Hz), 124.4, 123.3 122.8 (2C, q, $^3J_{CF}$ = 3.8 Hz), 116.3 (2C), 115.9 (2C), 115.3 (2C), 68.7, 68.4, 26.7 (6C), 26.2 (2C); CI+ mass spectrum, *m/z* (%): 514 ([MH^+], 100).

(E)-4-(10-(4-((4-(Trifluoromethyl)phenyl)diazenyl)phenoxy)decyloxy)benzendiazonium tetrafluoroborate (1) To a solution 340 mg (1.20 mmol) of the azobenzene aniline **1d** in 20 mL of THF was added 0.50 mL (3.60 mmol) of $BF_3 \cdot OEt_2$ at -40 ℃. The mixture was stirred for 20 min and then 0.30 mL (2.40 mmol) of *tert*-BuONO was added dropwise. The mixture was stirred for 10 min and then gradually warmed to room temperature. Anhydrous ether was added to precipitate the diazonium salt. The mixture was filtered and the salt copiously washed with ether to give 350 mg (76% yield) of the diazonium salt **1**: FTIR (KBr) 2921, 2851, 2260, 1566, 1406, 1290, 1064, 849 cm^{-1}; ^1H NMR (300 MHz, Acetone-d_6) δ 8.73 (2H, d, J = 9.4 Hz), 8.03 (2H, d, J = 8.4 Hz), 7.94 (2H, d, J = 9.4 Hz), 7.89 (2H, d, J = 8.4 Hz), 7.50 (2H, d, J = 9.4 Hz), 7.13 (2H, d, J = 9.4 Hz), 4.38 (2H, t, J = 6.5 Hz), 4.12 (2H, t, J = 6.5 Hz), 1.91-1.79 (4H, m), 1.51-1.35 (12H, m); ^{13}C NMR (75.5 MHz, acetone-d_6) δ 170.3, 163.6, 155.7, 147.4, 137.1 (2C), 127.2 (q, $^2J_{CF}$ = 22.7 Hz), 125.9 (q, $^1J_{CF}$ = 271 Hz), 125.8 (2C), 125.8 (2C), 123.8, 123.6 (2C), 115.8 (2C, q, $^3J_{CF}$ = 3.8 Hz), 103.2 (2C), 71.4, 69.2 (2C), 29.8 (6C), 26.7 (2C).Elemental analysis: Calcd. For $C_{29}H_{32}BF_7N_4O_2$: C, 56.88; H, 5.27; N, 9.15. Found: C, 56.76; H, 5.34; N, 9.08.



Scheme S2. Synthesis of the azobenzene diazonium salts **2** and **3**.

1-Nitroso-4-trifluoromethyl-benzene (2b) To a solution 4 g (24.8 mmol) of 4-(trifluoromethyl)aniline in 35 mL of CH_2Cl_2 was added 46 g (74.4 mmol) of OXONE® in 200 mL of H_2O. The mixture was stirred for 12 h room temperature. Water was then added and the aqueous layer was extracted with CH_2Cl_2 three times. The organic layer were washed with 1N HCl, Saturated $NaHCO_3$ solution, dried over $MgSO_4$ and concentrated under reduced pressure copiously to give 3.5 g (81% yield) of nitrosobenzene **2b**.

(E)-4-((4-(Trifluoromethyl)phenyl)diazenyl)aniline (2c) To a solution 2.50 g (14.3 mmol) of the nitrosobenzene **2b** in 40 mL of AcOH was added 1.90 g (17.6 mmol) of 1,4-phenylenediamine at room temperature. The mixture was stirred for 19 h. Water was then added and the aqueous layer was separated and extracted with CH_2Cl_2 three times. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with 30% ethyl acetate in hexanes gave 1.0g (26% yield) of the azobenzene aniline **2c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.91(2H, d, J = 8.5 Hz), 7.83 (2H, d, J = 8.8 Hz), 6.74 (2H, d, J = 8.5 Hz), 4.00 (2H, brs).

(E)-4-((4-(Trifluoromethyl)phenyl)diazenyl) benzendiazonium tetrafluoroborate (2) To a solution 300 mg (1.13 mmol) of the azobenzene **2c** in 20 mL of THF was added 480 mg (3.38 mmol) of $BF_3 \cdot OEt_2$ at -40 ℃. The mixture was stirred for 20 min and then 240 mg (2.31 mmol) of *tert*-BuONO was added dropwise. The mixture was stirred for 10 min and then gradually warmed to room temperature. Anhydrous ether was added to precipitate the diazonium salt. The mixture was filtered and the salt washed with ether copiously to give 290 mg (70% yield) of diazonium salt **2**: FTIR (KBr) 3089, 2282, 1575, 1415, 1323 1064 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.90 (2H, d, J = 9.0 Hz), 8.36 (2H, d, J = 9.0 Hz), 8.17 (2H, d, J = 8.4 Hz), 8.04 (2H, d, J = 8.4 Hz); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 157.7, 154.4, 133.1 (2C), 133.5 (q, $^2J_{CF}$=32.6 Hz), 127.7 (2C, q, $^3J_{CF}$= 3.8 Hz), 125.4(2C), 125.3 (2C), 124.3 (q, $^1J_{CF}$= 271 Hz), 123.4; Elemental analysis: Calcd. For $C_{13}H_8BF_7N_4$: C, 42.89; H, 2.22; N, 15.39. Found: C, 42.71; H, 1.93; N, 15.30.

(E)-4-(Phenyldiazenyl)benzendiazonium tetrafluoroborate (3) To a solution 550 mg (2.78 mmol) of the 4-aminoazobenzene **3a** in 22 mL of THF was added 1.19 g (7.61 mmol) of $BF_3 \cdot OEt_2$ at -40 ℃. The mixture was stirred for 20 min and then 580 mg (5.10 mmol) of *tert*-BuONO was added dropwise. The mixture was stirred for 10 min and then gradually warmed to room temperature. Anhydrous ether was added to precipitate the diazonium salt. The mixture was filtered and the salt washed with ether copiously to give 500 mg (61% yield) of diazonium salt **3**: FTIR (KBr) 2293, 1575, 1310, 1068, cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.84 (2H, d, J = 8.5 Hz), 8.30 (2H, d, J = 8.5 Hz), 8.01 (2H, d, J = 8.4 Hz), 7.70 (3H, m); Elemental analysis: Calcd. For $C_{12}H_9BF_4N_4$: C, 48.69; H, 3.06; N, 18.93. Found: C, 48.60; H, 2.94; N, 18.75.

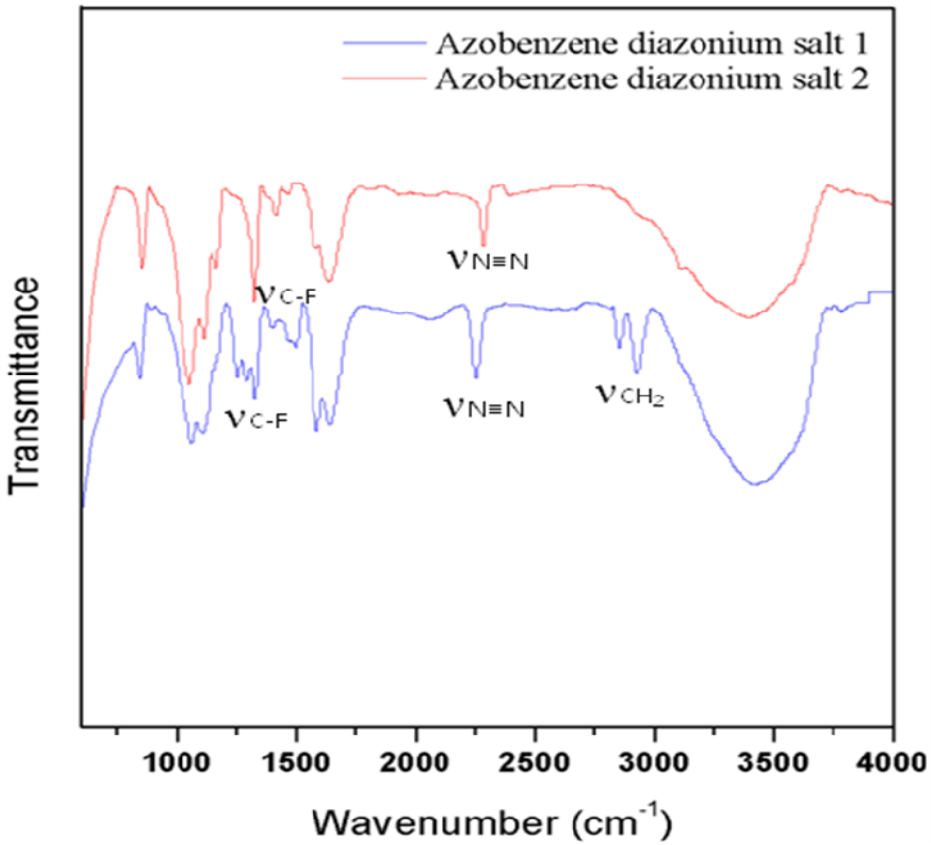
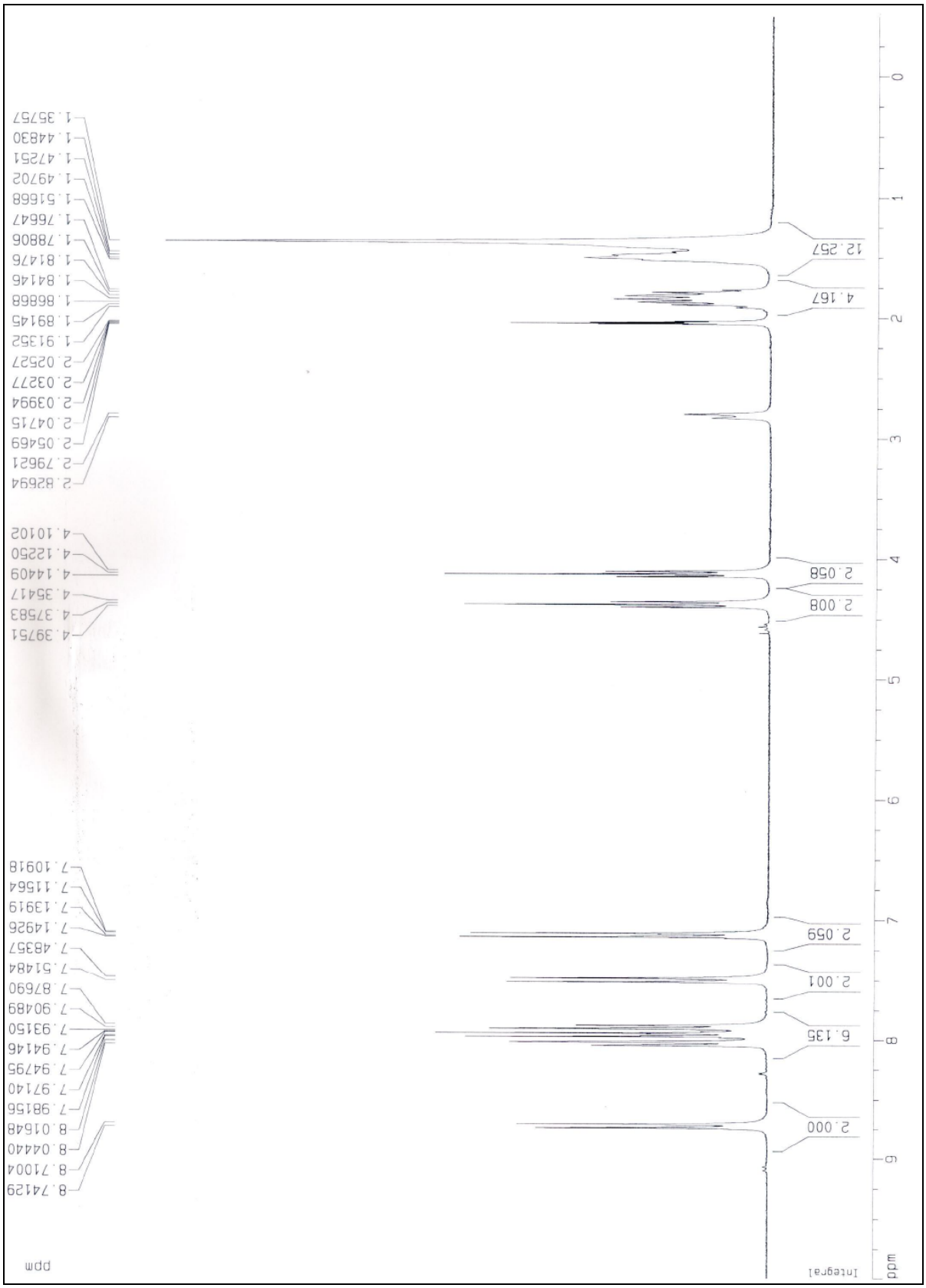


Fig. S1. FT-IR Spectra of Azobenzene diazoniumsalts **1** and **2**.

a)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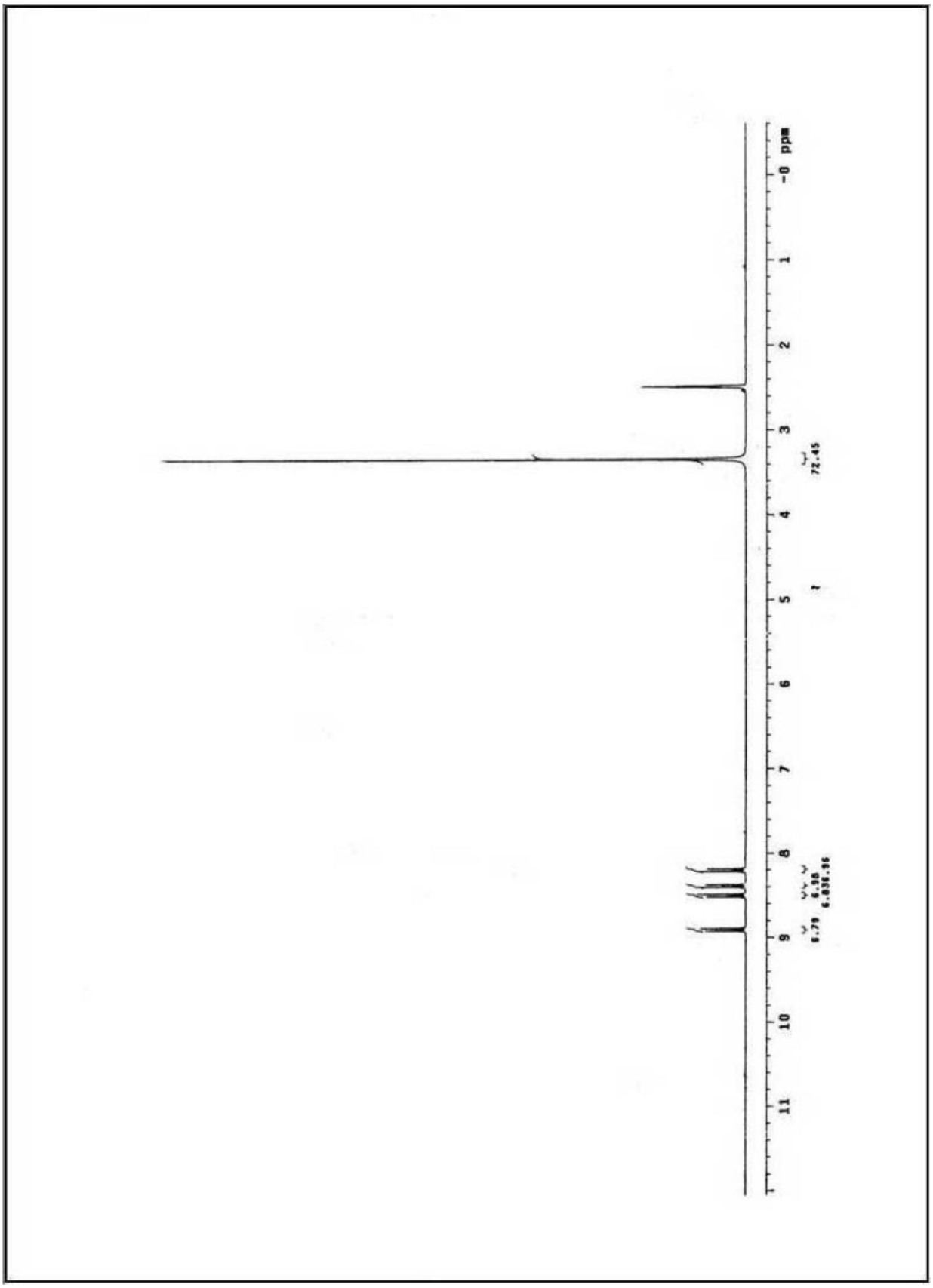
b)



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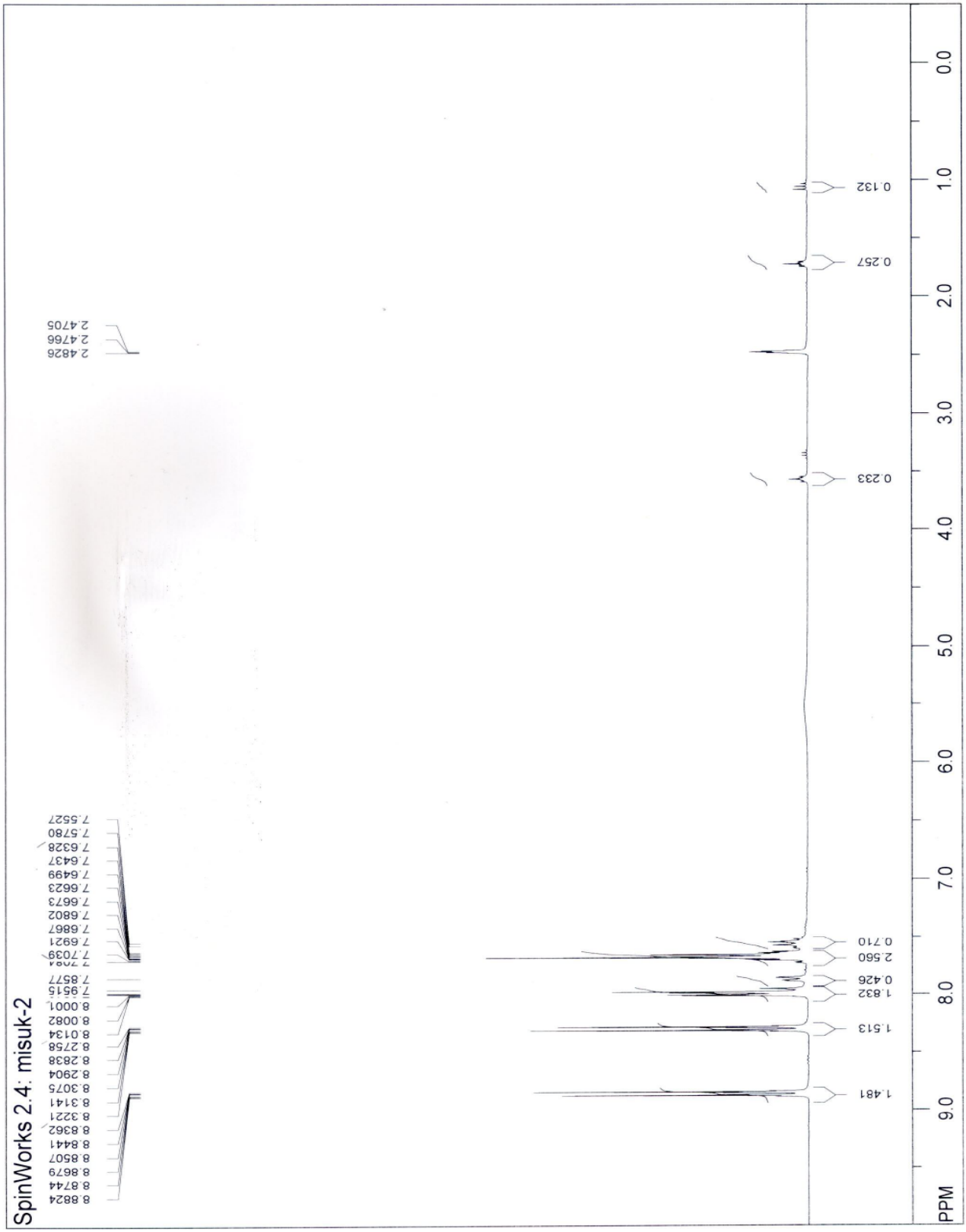

Fig. S2. ^{1}H NMR Spectra of Azobenzene diazoniumsalts **1** (a), **2** (b) and **3** (c)

Photo-isomerization of the azobenzene diazonium salt 2 in CH_3CN. To estimate the parameters controlling the photoisomerization of the functionalized substrate, a spectroscopic study of azobenzene diazonium salt **2** was performed. Azobenzene diazonium salt **2** in CH_3CN solution (25 μM) was irradiated by alternate illumination with UV light centered at 360 nm and visible light centered at 430 nm[2]. Azobenzene diazonium salt **2** for irradiation time at 430 nm after irradiation at 360 nm for 5 min. The azobenzene diazonium salt **2** exhibited a UV-vis absorption spectra similar to methylene-spaced aryl azobenzene diazonium salt **1** in CH_3CN, showing an absorption maxima at near 330 nm and a weak band at near 474 nm, which again, corresponding to the π-π* and n-π* transition bands of the *trans* azobenzene respectively. Upon UV irradiation over 30 min the intensity of the π-π* transition band at 330 nm greatly decreased while that of the n-π* transition band at 474 nm slightly increased (*trans* isomerization to *cis*) Upon visible irradiation over 30 min the intensity of the π-π* transition band at 330 nm increased showing the *cis* isomerization *trans*. Upon UV and visible irradiation the changes in the UV/Vis absorption spectra of the azobenzene diazoniumsalt **2** in CH_3CN was observed.

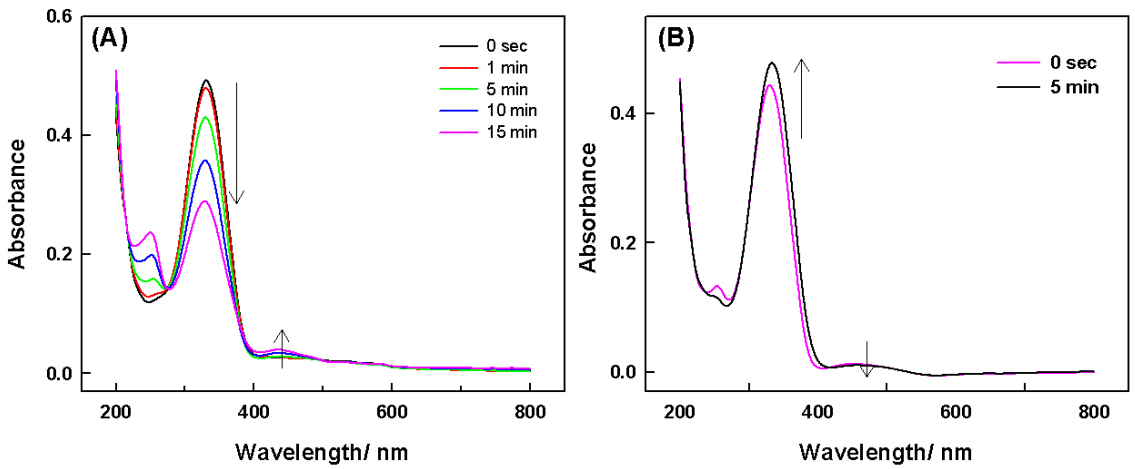

Fig. S3. UV-Vis absorption spectra of the azobenzene diazonium salt **2** solution in CH_3CN as irradiation time (A) at 360 nm and (B) at 430 nm after irradiation at 360 nm for 5 min.

Preparation of a self-assembly monolayer (SAM) of azobenzene-Modified Si(111) surfaces. The wafer was then hydride-terminated Si wafer was prepared according to literature procedures.[3] For Si(111), this etching condition was known to create a well-ordered mono hydride silicon surface. The Si(111) wafers were first ultrasonically cleaned in acetone followed by chloroform (10 min each) and were then were oxidized in 3:1 concentrated H_2SO_4/30% H_2O_2 for 15 min. The oxidized samples were then immersed in a nitrogen-sparged 40% aqueous NH_4F solution for 15 min. The silicon was rinsed thoroughly with deionized water and blown-dried under a stream of nitrogen gas after each step. For Si(111), this etching condition was known to create a well-ordered mono hydride silicon surface. The cleaned Si(111) plates were directly used for preparation of self-assembled monolayers of the azobenzene diazoium salts in a glove box. For the assembly procedure, a cleaned surface is was exposed to a solution of the azobenzene diazonium salt in anhydrous CH_3CN (0.15 mM), in the glove box, over a period of 3 h and under an inert atmosphere. The silicon wafer was then sonicated for 1 min, rinsed thoroughly with deionized water and blown-dryied under a stream of N_2 gas.[3]

The reaction time for the complete monolayer was somewhat slower than that for the azobenzene diazonium salt **2** assembly. According to the reaction time the thickness value was 26.57 Å (1 h) and 27.36 Å (2 h)

The optimum assembly time for the completed monolayer was 3 h as the measured thickness value (31.92 Å) reaches the theoretical value (30.87 Å). The multilayer formation was also sluggish in prolong assembly time. The measured contact angle showed that the surface to be hydrophobic as expected from the hydrophobic nature of the methylene-spaced aryl azobenzene diazonium salt **1**.

[2] X. Zhang et al. *J. Phys. Chem. C* 2008, **112**, 8288

[3](a) M. P. Stewart, F.Maya, D.V. Kosynkin, S. M. Dirk, J. J. Stapleton, C.L. McGuiness, D.L. Allara and J. M. Tour, *J. Chem. Soc.* 2004, **126**, 370 (b) B. Chen, A. K. Flatt, H.Jian, J. L. Hudson and J. M. Tour, *Chem.Mater.* 2005, **17**, 4832

Analysis of Water contact angle measurements

The trifluoromethyl group is a hydrophobic group, based on water contact angle measurement.[4] Water contact angle were measured after 30 min of exposure. With irradiation with UV light (360 nm) for 30 min, the photochemical change from *trans* to *cis* form caused a change in wattability reflected in a water contact angle(Θ) change, while it is completely reversed to the original value by 30 min irradiation with visible light (430 nm). For compound **1**, water contact angle(θ) was changed from 87.82° (*trans* form) to 82.74° (*cis* form), giving repeated cycles with nearly a 5° difference in wettability upon UV/vis irradiation as shown in Table S**1**. For a control experiment, the water contact angle of compound **2** having no aliphatic $–CH_2$-chain was changed from 79.12° to 74.83°, giving 4 degree difference in photoswitching ON/OFF ratio. For another control experiment, compound **3** having no aliphatic $–CH_2$-chain and H-substituent instead of the trifluoromethyl group was changed from 74.56° to 72.24°, producing only 2 degree difference in photoswitching ON/OFF ratio). For the control experiments, however, only less than 2 cycles in the contact angle measurement were found, indicating that isomerization on the surface is not as stable as observed in the solution phase.

Table. S**1**. Change in the water contact angle of the functionalized SAM grafted by the compounds **1**, **2** and **3** at the reported alternative irradiation at 360 nm and 430 nm.

Irradiation	**Initial**	**UV**	**vis**	**UV**	**vis**	**UV**	**vis**	**UV**	**vis**	**UV**	**vis**
WCA(Θ) of compound **1**	87.82	82.74	87.54	82.30	86.94	82.17	86.22	82.00	86.94	82.89	86.95
WCA(Θ) of compound **2**	79.12	74.83	78.95	74.55	75.24						
WCA(Θ) of compound **3**	74.56	72.24	74.16	72.31	73.20						

[4] H. S. Lim, J. T. Han, D. H. Kwak, M. H. Jin and K.W. Cho *J. Am. Chem. Soc.* 2006, **128**, 14458.

Analysis of XPS. In the XPS spectra of azobenzene diazoniumsalt films 1 and 2, C 1s spectrum was observed at 285.1 and 292.9 eV, assigned to $-CH_2$ and $-CF_3$, respectively. And an N 1s peak (400.5 eV) and a F 1s (688.4 eV) peak also detected, confirming the presence of -N=N- and $-CF_3$ groups. Clearly, the absence of the BF_4 counterion which composes part of the diazonium salt (typically appearing at about 686.5 eV) is evidenced.

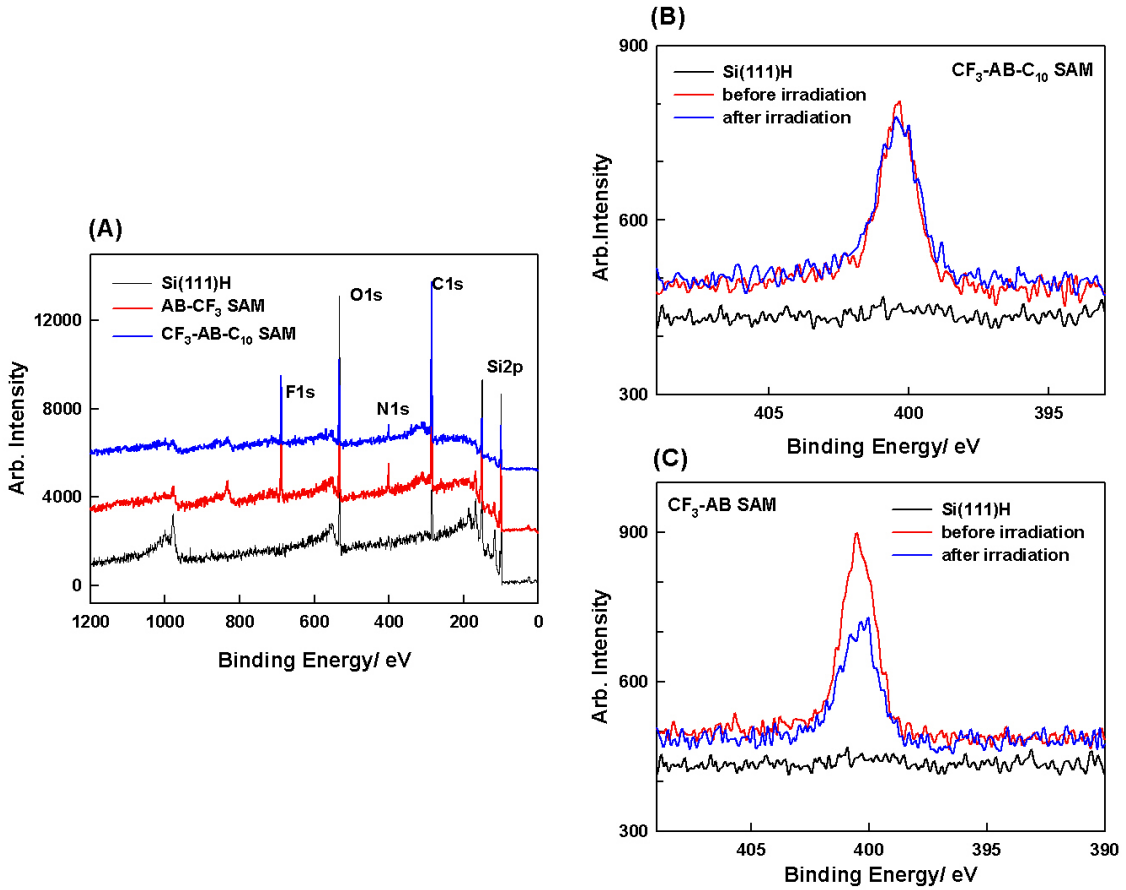

Fig. S4. (A) XPS survey spectra of SAMs **1** and **2** on Si(111)H. (B) and (C) enlarged N 1s spectra of SAMs **1** and **2** before and after several irradiations (over 10 times) at 360 nm for 30 min, respectively.