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## A photoswitchable methylene-spaced fluorinated aryl azobenzene monolayer grafted on silicon<sup>†</sup>

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Aryldiazonium-terminated methylene-spaced trifluoromethylazobenzene derivatives have been synthesized. Their selfassembled monolayers (SAMs) on a silicon surface allow for a stable and reversible molecular photoswitch.

With the advent of molecular photoelectronic devices for future applications in microelectronics and bioelectronics,<sup>1,2</sup> development of functionalized and robust organic monolayers that can be directly grafted onto silicon substrates *via* liquid phase reactions is essential. The covalent bonding between the silicon substrate and the carbon atom of the organic molecules makes them very stable, even under harsh conditions (*i.e.* sonication in organic solvents and boiling water temperature).<sup>3,5</sup> This constitutes a key advantage when compared with self-assembled monolayers (SAMs) of organic thiols on gold surfaces whose stability seems less sound and subordinate to several factors.<sup>4</sup> For these reasons, the direct covalent grafting of alkyl-tailed azobenzenes, with the help of light and catalysts, onto a hydride-passivated silicon surface has been reported.<sup>5</sup>

In recent years, air-stable and easily synthesized aryldiazonium salts have provided organic monolayers that encourage strong bonds between the carbons of  $\pi$ -conjugated organic molecules and surface atoms.<sup>6</sup> In particular, the noble method provides spontaneous and room-temperature routes to direct covalent bonds.

Until now, however, important issues such as the steric constraints of *trans/cis* isomerization of the azobenzene, excited-state quenching, and stability of the covalently grafted SAMs on the silicon surface have not been addressed for full realization of photo-driven molecular switching devices.<sup>7</sup>

In this communication, a novel aryldiazonium-terminated methylene-spaced trifluoromethylazobenzene **1** was synthesized and its reversibly photoswitchable SAMs on a silicon surface were characterized. To the best of the authors' knowledge, this is the first reported observation of direct photoswitching of an azobenzene SAM covalently grafted with an aryl carbon on a silicon surface without even use of a mixed SAM.<sup>7</sup>

The aryldiazonium salt was designed for direct attachment to the silicon surface to simultaneously provide a phenyl space

to prevent the steric constraints of photo-induced trans/cis isomerization of the azobenzene SAMs. The methylene-spaced alkyl chains of compound 1 were adopted for generating high-ordered SAMs by using van der Waals interaction of the neighboring alkyl chains, as well as suppressing the excited-state surface quenching caused by the electronic coupling between the molecule and substrate during irradiation of the azobenzene SAM on the silicon substrate. Additionally, the hydrophobic trifluoromethyl group was introduced to increase the photo-switching ON/OFF ratio measured for the hydrophilic water drop using the water contact angle (WCA) method (see ESI<sup>†</sup> for control experiments with compounds 2 and 3)<sup>8</sup> and to protect the degradation of the fluorinated SAMs from the photo irradiation since the bond dissociation energy of C-F ( $\sim 130 \text{ kcal mol}^{-1}$ ) is much higher than that of the C-H bond.9

For compounds 1, 2 and 3 shown in Fig. 1 (see ESI<sup> $\dagger$ </sup>, Schemes S1 and S2), *para*-nitrophenol was dimerized by addition of dibromodecane in the presence of Cs<sub>2</sub>CO<sub>3</sub>. The resultant dinitrobenzene was then reduced to dianiline. Addition of trifluoromethylnitrosobenzene to the dianiline in the presence of acetic acid afforded the monoazobenzene, which was then diazotized to give azobenzene diazonium salt 1 in 76% overall yield. Compound **2** was prepared according to literature procedures in 70% yield.<sup>10</sup>

Upon UV and visible light irradiation, shown in Fig. 2, changes in the UV-Vis absorption spectra of compound 1 in CH<sub>3</sub>CN were observed (see ESI<sup>†</sup>). Compound 1 exhibited its absorption maxima near 316 nm with a weak band at about 437 nm, corresponding to the  $\pi$ - $\pi$ \* and n- $\pi$ \* transition bands of the *trans* azobenzene, respectively. Upon UV irradiation over 10–20 min, the intensity of the  $\pi$ - $\pi$ \* transition band at 316 nm decreased while the n- $\pi$ \* transition band at 437 nm slightly increased (*trans* to *cis* isomerization). Reversibly, upon visible irradiation over 15 min, the intensity of the  $\pi$ - $\pi$ \* transition band at 316 nm decreased (*cis* to *trans* isomerization).



Fig. 1 Molecular structures of photoswitches investigated.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Details of synthesis of azobenzene diazonium salt, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, UV-Vis, FT-IR, and XPS of the azobenzene diazonium salt. See DOI: 10.1039/c0cc00521e



Fig. 2 UV-Vis absorption spectra of the compound 1 solution (CH<sub>3</sub>CN) as irradiation time (A) at 360 nm and (B) at 430 nm after irradiation at 360 nm for 10-15 min.

Compound 2 exhibited a UV-Vis absorption spectrum similar to compound 1 in CH<sub>3</sub>CN, showing an absorption maximum at about 330 nm and a weak band near 474 nm. This also corresponds to the  $\pi$ - $\pi^*$  and n- $\pi^*$  transition bands of the *trans* azobenzene, respectively. Upon UV irradiation over 30 min, the intensity of the  $\pi$ - $\pi^*$  transition band at 330 nm greatly decreased while that of the n- $\pi^*$  transition band at 474 nm slightly increased (*trans* to *cis* isomerization). Upon visible irradiation over 30 min, the intensity of the  $\pi$ - $\pi^*$ transition band at 330 nm increased, showing the *cis* form isomerizing to the *trans* form (see ESI<sup>†</sup>, Fig. S3). The spectra of compounds 1 and 2 in solution exhibited the photoisomerization as previously reported for the azobenzene-type molecule.<sup>11</sup>

For the azobenzene monolayer, the hydride-terminated silicon surface was first prepared according to literature procedures.<sup>6a</sup> The hydride-terminated silicon surface was then exposed to the solution of the compounds **1** and **2** in anhydrous CH<sub>3</sub>CN (0.15 mM) during a period of 2 to 3 h, in a glove box and under an inert atmosphere (see ESI†). The measured ellipsometric thicknesses of the modified film were approximately  $3.19 \pm 0.06$  and  $1.81 \pm 0.07$  nm for compound **1** and **2** SAMs, respectively. These thickness values were similar to the estimated value of a monolayer, 3.09 and 1.31 nm for compounds **1** and **2**. The molecular length was estimated using Cambridge Scientific Chem 3D.

The elemental composition of the azobenzene-modified Si(111) surface was examined by XPS. Elements C, N, O, F, and Si were monitored in the spectra (see ESI<sup>†</sup>, Fig. S4). In the XPS spectra of the compound **1** film, the C 1s spectrum was observed at 285.0 and 292.8 eV, and assigned to  $-CH_2$  and  $-CF_3$ , respectively. An N 1s peak (400.3 eV) and an F 1s (688.6 eV) peak were also detected, confirming the presence of -N = N- and  $-CF_3$  groups.

Photoisomerization *via* irradiation with a high-intensity UV and visible light can be achieved to give the *trans* or *cis* form, which can be utilized for a photoswitching. The contact angle measurements were employed to observe the changes of surface wettability of a self-assembled monolayer after UV and visible light irradiation since the hydrophobicity of the *trans* state exposed to a hydrophobic  $-CF_3$  group is a little higher than that of the *cis* state.<sup>5,8</sup> Thus, it is expected that the contact angle of the *trans* monolayer increases, while that of the *cis* monolayer deceases because of its higher dipole moment and weaker hydrophobicity. Water contact angles were measured after 30 min of exposure. With irradiation with



Fig. 3 A representation of the photoswitching of the azobenzene monolayer of compound 1.

UV light (360 nm) for 30 min, the photochemical change from *trans* to *cis* caused a change in wettability reflected in a water contact angle ( $\theta$ ) change from 87.82° to 82.74°, while it is completely reversed to the original value by 30 min irradiation with visible light (430 nm). This kind of cycle can be performed repeatedly with nearly a 5° difference in wettability upon UV/vis irradiation as shown in Table S1.† Fig. 3 shows the scheme of the effects of *trans-cis* isomerization on the relative protrusion of the azobenzene monolayer.

For the SAMs of compounds 2 and 3, however, only less than 2 cycles in the contact angle measurement for the repeated UV and visible light irradiation were found (see ESI<sup>+</sup> for control experiments with compounds 2 and 3), indicating that isomerization on the surface is not as stable as observed in the solution phase. It is known that evidence of photoinduced switching of single molecules on metal electrodes is often complicated by surface quenching<sup>7</sup> and steric hindrance. The previous failure of the surface isomerization led to the design of new azobenzene diazonium salts bearing a molecular spacer to suppress excited-state quenching from the metal substrate<sup>7</sup> and form dense assemblies of single tethered azobenzene molecules, such as compound 1. In contrast to the SAM 2, azobenzene SAM 1 showed stable changes in surface properties after repeated UV and visible light irradiation. This kind of cycle can be performed repeatedly with nearly a 5° difference in wettability. The reversible switching was again repeated many times, and good reversibility of the surface wettability was observed as depicted in Fig. 4.

To verify the stability of SAM 1 to UV and visible light irradiation, the N 1s XPS spectra were investigated. After several UV light irradiations, each for 30 min, the intensities of the N 1s peak from -N=N- remained unchanged, indicating that the methylene-spaced azo monolayer was not damaged during UV light irradiation even after 60 days (see ESI<sup>†</sup>, Fig. S4(B)). However, the intensities of the N 1s peak of SAM 2 decreased after several UV light irradiations (see ESI<sup>†</sup>, Fig. S4(C)). Thus the methylene spacer plays an important role in the stability of the SAM under UV light irradiation.



**Fig. 4** Evolution of the water contact angle of the azobenzene monolayer **1** with the methylene-spaced group. The columns labeled *cis* and *trans* respectively refer to the sample after UV (360 nm) and visible (430 nm) light irradiation.

This stability was also tested through WCA.<sup>12</sup> The wettability showed no obvious changes in laboratory ambient conditions for over 60 days even though the intensities of the ON/OFF ratio were slightly reduced, demonstrating not only the stability of the grafted monolayer, but also the reproducibility of the isomerization performance of the azobenzene molecule.<sup>5</sup>

In conclusion, a novel aryldiazonium-terminated trifluoromethylazobenzene bearing a carbon chain between the azobenzene moiety and silicon surface (111) was successfully prepared and provided a stable monolayer that prevented possible surface quenching during irradiation of the azobenzene SAM on the silicon substrate. A self-assembled monolayer of a novel methylene-spaced fluorinated molecule was quite stable with photo irradiation over a couple of months. The wettability study demonstrated the *trans/cis* conformational transformation that overcame the steric constraints, even after repeated cycles lasting several months in a laboratory environment. The novel use of the methylene-spaced fluorinated stable SAMs on sillicon surfaces is applicable in developing miniaturized optical switches.

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