

## **Supporting Information**

**for**

### **Reversible On/Off Conductance Switching of Single Diarylethene Immobilized on a Silicon Surface**

Kazuki Uchida, Yoshinori Yamanoi, Tetsu Yonezawa, and Hiroshi Nishihara\*

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku,  
Tokyo 113-0033, Japan.

#### **Contents**

<b>1. General</b>	<b>S2</b>
<b>2. Copy of <math>^1\text{H}</math> &amp; <math>^{13}\text{C}</math> NMR spectra of 1o</b>	<b>S3</b>
<b>3. UV-vis spectra</b>	<b>S5</b>
<b>4. AFM images</b>	<b>S5</b>

## 1. General

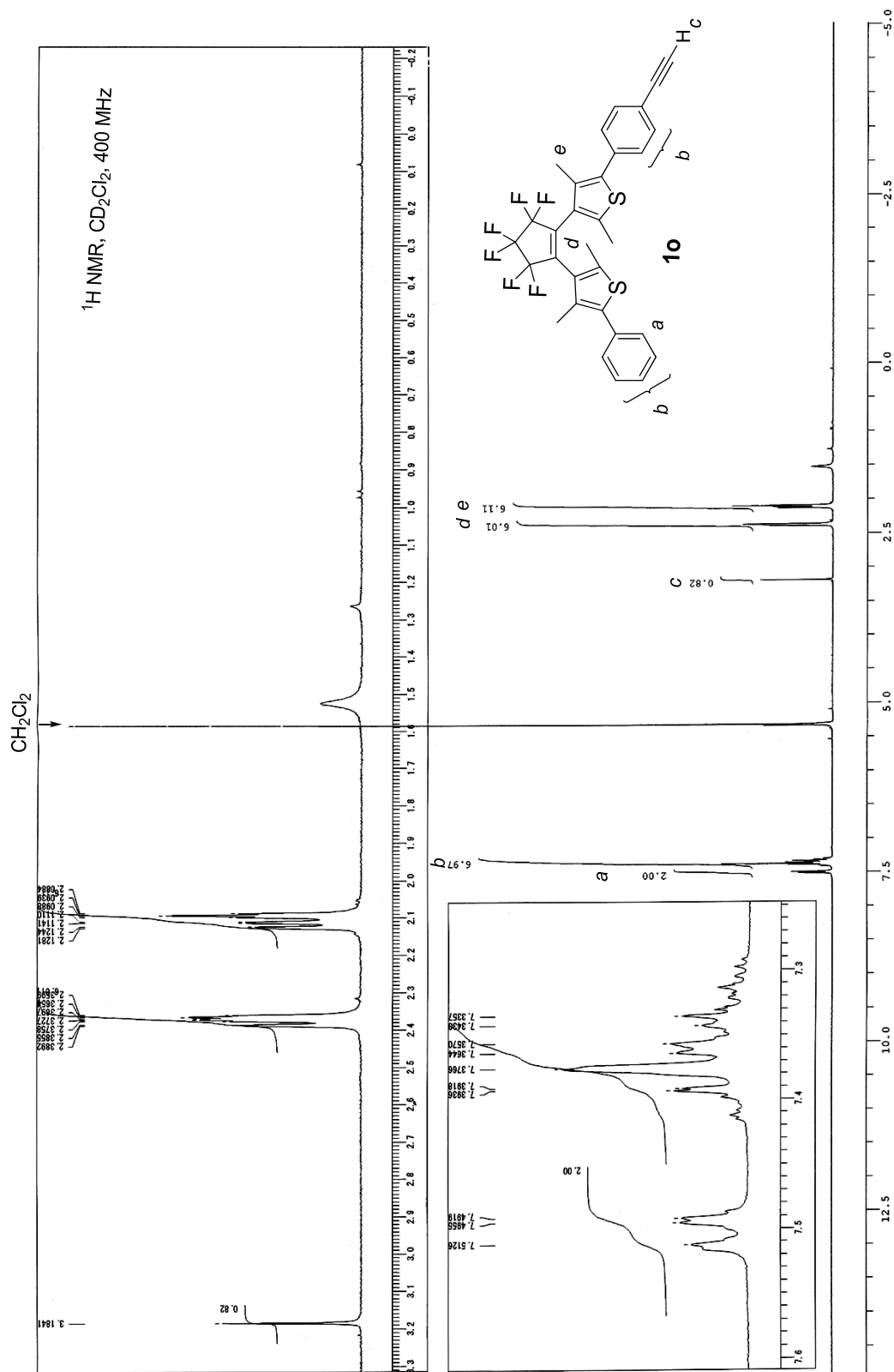
**Materials.** P-type silicon wafers (boron doped) with (111) orientation were obtained from Taku Material Corporation (1.30-2.97  $\Omega\text{cm}$ ). THF was distilled from sodium benzophenone ketyl under nitrogen. Water (18.2 M $\Omega\text{cm}$ ) was purified using a Millipore Milli-Q water system. All other reagents were used directly as supplied. All experiments were conducted under an argon atmosphere in glassware dried under vacuum.

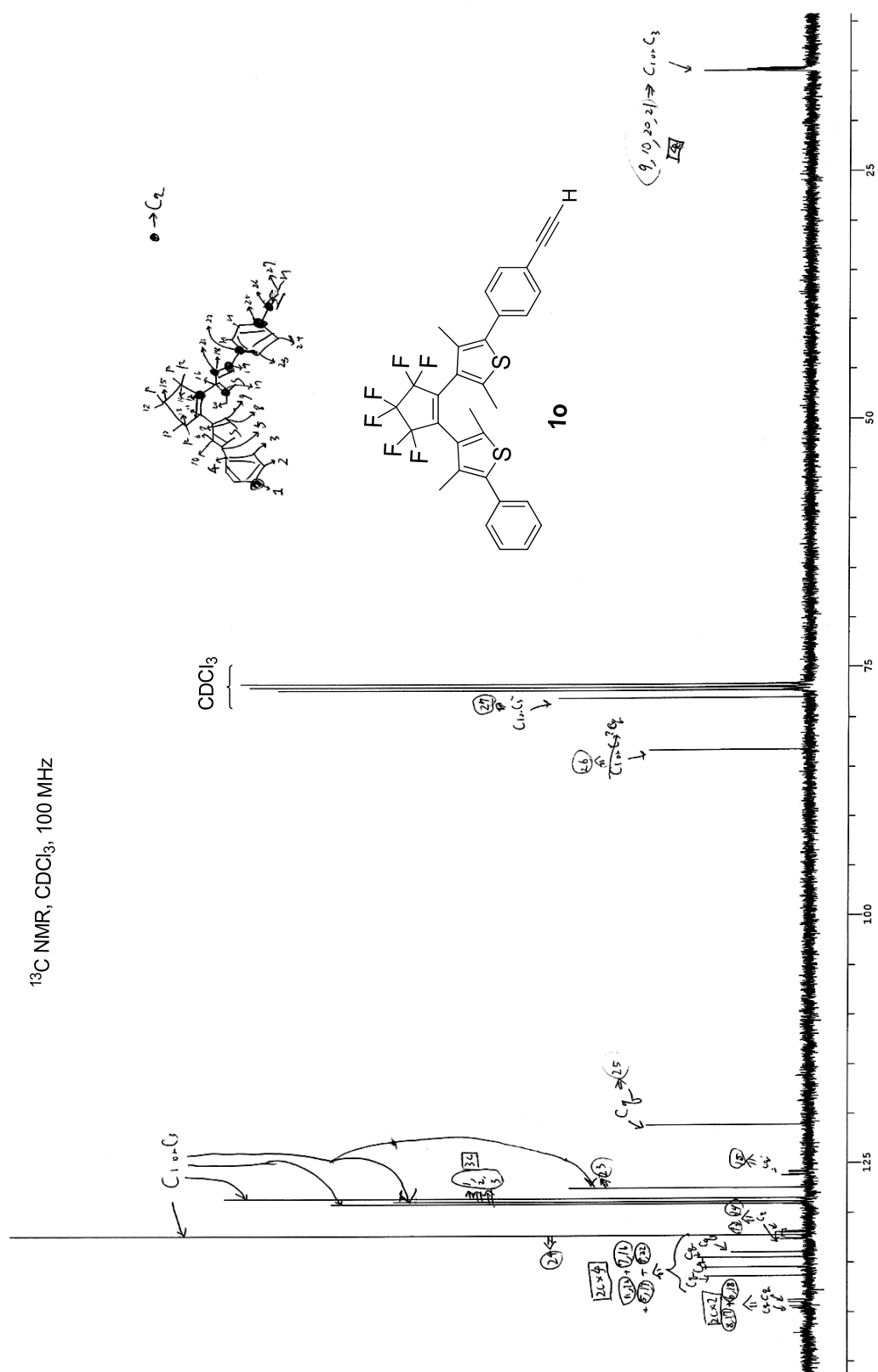
**Surface Preparation.** The freshly etched hydrogen-terminated silicon(111) wafers and **1o** (20.9 mg, 0.036 mmol) were placed into a Schlenk flask. Distilled toluene (10 mL) was added to the flask, and the mixture was refluxed for 18 h. After the reaction, the sample was removed, rinsed with toluene and sonicated successively in toluene, ethanol and Milli-Q water. The modified silicon wafers were dried under a stream of argon gas.

**Surface Characterization.** AFM measurements were recorded by using an SII SPA300HV Seiko Instrument using SPI 3800N Probe Station in vacuo with a rhodium coated cantilever ('SI-DF3-R',  $f = 27$  kHz,  $C = 1.4$  N/m). Contact angle measurements were obtained with a FACE Contact-Angle Meter (Model: CA-DT) at room temperature. Contact angles were measured from sessile water droplets dropped from a syringe needle onto the surface. This measurement was repeated ten times and results were averaged.

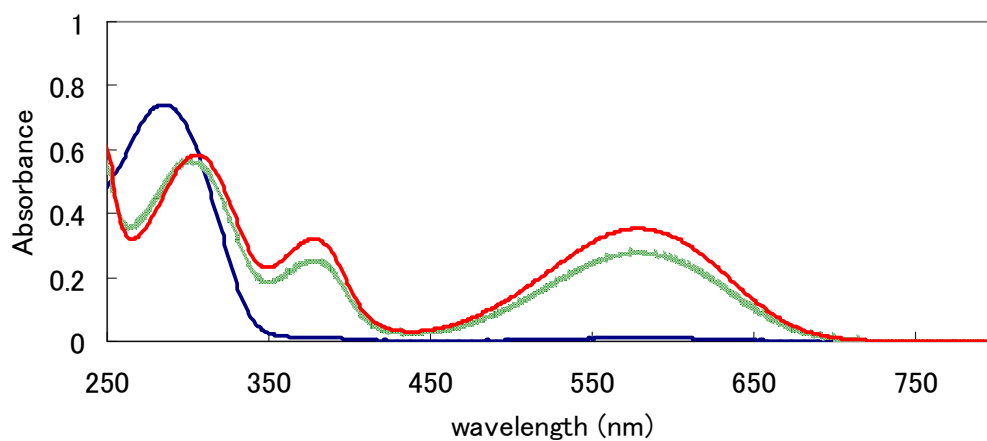
**1-(2,4-Dimethyl-5-(4-ethynylphenyl)-3-thienyl)-2-(2,4-dimethyl-5-phenyl-3-thienyl)heptafluorocyclopentene (1o).** This compound was synthesized according to the following method. *n*-Butyllithium (1.3 mL, 3.3 mmol, 2.64 M hexane solution) was added to a solution of 3-bromo-2,4-dimethyl-5-(4-trimethylsilylethynylphenyl)thiophene **2** (1.09 g, 3.0 mmol) in THF (60 mL) at  $-78$  °C, and stirred at that temperature for 1 h before addition of 1-(2,4-dimethyl-5-phenyl-3-thienyl)heptafluorocyclopentene (1.14 g, 3.0 mmol). After stirring for 3 h at  $-78$  °C, the reaction mixture was allowed to warm to room temperature. The reaction mixture was poured into water to quench the reaction, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate three times. The combined extracts were dried over sodium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel to provide compound **3** (1.41 g, 73%). Compound **3** (1.00 g, 1.55 mmol) was dissolved in diethyl ether (60 mL). To this solution was added potassium carbonate (320 mg, 2.3 mmol) in methanol (140 mL), followed by stirring at room temperature for 24 h. The reaction mixture was poured into water to quench the reaction, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate three times. The combined extracts were dried over sodium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel to give the desired compound **1o** (840 mg, 95%). Mp  $63.0$ – $65.0$  °C;  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  2.06–2.16 (m, 6H), 2.33–2.42 (m, 6H), 3.18 (s, 1H), 7.28–7.43 (m, 7H), 7.48–7.53 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  14.5–15.0 (m, 4CH<sub>3</sub>), 78.1 (CH), 83.3 (C<sub>q</sub>), 121.1 (C<sub>q</sub>), 126.0 (q,  $J = 34.6$ , 8.2 Hz, C<sub>q</sub>), 127.5 (CH), 128.5 (CH), 128.9 (CH), 129.1 (CH), 132.2 (d,  $J = 69$  Hz, C<sub>q</sub>), 132.3 (CH), 132.3 (d,  $J = 68$  Hz, C<sub>q</sub>), 133.9 (2C<sub>q</sub>), 134.5 (2C<sub>q</sub>), 135.4 (2C<sub>q</sub>), 136.3 (2C<sub>q</sub>), 138.9 (d,  $J = 24$  Hz, 2C<sub>q</sub>), 139.5 (d,  $J = 21$  Hz, 2C<sub>q</sub>); EI-MS  $m/z = 572$  ( $\text{M}^+$ ); Anal. Calcd. for  $\text{C}_{31}\text{H}_{22}\text{S}_2\text{F}_6$ : C, 65.02; H, 3.87. Found: C, 65.00; H, 3.97.

2. Copy of  $^1\text{H}$  &  $^{13}\text{C}$  NMR spectra of 1o



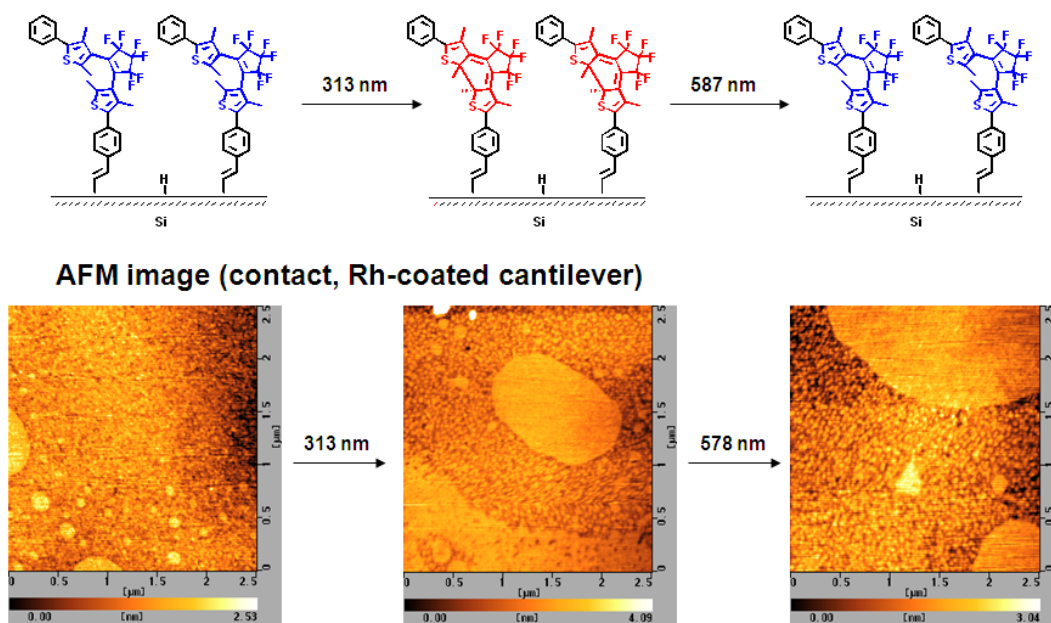
<sup>13</sup>C NMR, CDCl<sub>3</sub>, 100 MHz

## 2. UV-vis spectra



**Figure S1.** Absorption spectra open-ring (Blue line) and closed-ring (Red line) isomers and photostationary state (Green mesh) by irradiation at 313 nm. Red line spectrum was calculated from blue line and green mesh spectra on the assumption that photostationary state was composed of 22% open-ring isomer and 78% closed-ring isomer.

## 3. AFM images



**Figure S2.** Tapping Mode AFM image of **1o**-Si SAM