

## Electronic Supplementary Information

# Tuning surface wettability through photocontrolled reversible molecular shuttle

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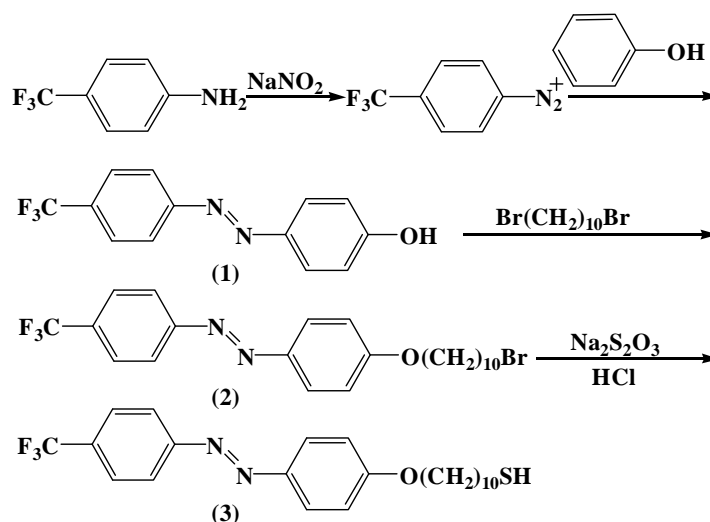
### Materials

1,10-dibromodecane,  $\alpha$ -cyclodextrin and 4-trifluoromethyl-phenylamine were purchased from Alfa Aesar and used without further purification. *n*-butanethiol (98%) was purchased from Lancaster. Aniline was redistilled under low-pressure before use. Other chemicals were analytical-grade reagents and were used as received. All aqueous solutions were prepared with deionized water.

### Characterization

$^1\text{H}$  NMR spectra were recorded on a JEOL JNM-ECA 300 (300 MHz) spectrometer. ESI-MS measurements were performed on a Thermo ELECTRON CORPORATION Finnigan LTQ with  $\text{CHCl}_3$  as the solvent. UV-vis spectra were performed on a Hitachi U-3010 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI Quantera SXM spectrometer with an Al  $K\alpha$  X-ray source. The base pressure in the XPS analysis chamber during spectral acquisition was  $6.7 \times 10^{-8}$  Pa.

### Synthesis of $\text{CF}_3\text{AzoSH}$ and $\text{AzoSH}$



Scheme S1. Synthetic routes of the  $\text{CF}_3\text{AzoSH}$ .

### Synthesis of 4-(4-(trifluoromethyl-phenylazo)-phenol (1)

Compound (1) was synthesized according to the literature.<sup>1</sup> <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 6.99 (2H, d, ArH ortho to phenolic OH), 7.85 (2H, d, ArH ortho to CF<sub>3</sub>) and 7.90-8.05 (4H, m, ArH ortho to –N=N–).

#### ***Synthesis of [4-(10-bromo-decyloxy)-phenyl]-(4-trifluoromethyl-phenyl)-diazene (2)***

Compound (2) was synthesized according to the literature.<sup>1</sup> <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 1.25-1.60 (12H, m, [CH<sub>2</sub>]<sub>4</sub>), 1.85 (4H, m, [CH<sub>2</sub>]<sub>2</sub>), 3.42 (2H, t, CH<sub>2</sub>Br), 4.08 (2H, t, CH<sub>2</sub>O), 7.03 (2H, d, ArH ortho to phenolic group), 7.75 (2H, d, ArH ortho to CF<sub>3</sub>) and 7.95 (4H, m, ArH ortho to –N=N–).

#### ***Synthesis of 10-[4-(4-trifluoromethyl-phenylazo)-phenoxy]-decane-1-thiol (3)***

Compound (3) was synthesized according to the literature.<sup>2</sup> <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 1.25-1.70 (12H, m, [CH<sub>2</sub>]<sub>4</sub>), 1.75-1.90 (4H, m, [CH<sub>2</sub>]<sub>2</sub>), 2.52 (d t, 2H, SCH<sub>2</sub>), 4.05 (2H, t, CH<sub>2</sub>O), 7.02 (2H, d, ArH ortho to phenolic group), 7.76 (2H, d, ArH ortho to CF<sub>3</sub>) and 7.95 (4H, m, ArH ortho to –N=N–). ESI-MS: m/z 439.26 [MH<sup>+</sup>].

#### ***Synthesis of 10-(4-phenylazo-phenoxy)-decane-1-thiol***

The same procedures were used to synthesize 10-(4-phenylazo-phenoxy)-decane-1-thiol (termed AzoSH). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 1.30-1.90 (16H, m, [CH<sub>2</sub>]<sub>8</sub>), 2.51 (d t, 2H, SCH<sub>2</sub>), 4.03 (2H, t, CH<sub>2</sub>O), 7.01 (2H, d), 7.47 (3H, m) and 7.91 (4H, m). ESI-MS: m/z 371.33 [MH<sup>+</sup>].

#### ***Preparation of the α-CD/CF<sub>3</sub>AzoSH inclusion complex solution<sup>3</sup>***

CF<sub>3</sub>AzoSH was dissolved in ethanol with concentrations of 1 × 10<sup>-5</sup> M. The aqueous solution of α-CD was prepared by using distilled water with concentrations of 5 × 10<sup>-4</sup> M. The α-CD/CF<sub>3</sub>AzoSH inclusion complex solution was prepared by sonicating the ethanol-water solution (1 : 9, v/v) of the mixture of α-CD (5 × 10<sup>-4</sup> M) and CF<sub>3</sub>AzoSH (1 × 10<sup>-5</sup> M) at 30 °C for 25 min (1 : 40, molar ratio).

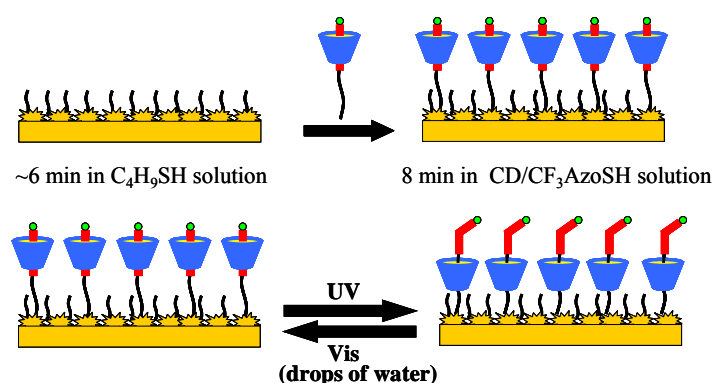
#### ***Preparation of the gold substrates***

After thorough cleaning procedures, quartz or glass substrates were precoated with 6 nm of chromium followed by 130 nm of high-purity gold, evaporated at a pressure of 5 × 10<sup>-6</sup> mbar from a resistively heated tungsten and molybdenum boat, respectively. After the substrates returned to room temperature slowly, the chamber was back-filled with high purity nitrogen. Hence, the gold-coated substrates were fabricated and ready for the preparation of SAMs.

#### ***Preparation of SAMs on gold substrates***

Before adsorption of the thiol monolayer according to the procedures reported previously,<sup>4</sup> the gold substrates were cleaned by immersing them in piranha solution (70 : 30 v/v 98% H<sub>2</sub>SO<sub>4</sub>/ 30 wt % H<sub>2</sub>O<sub>2</sub>) for 30 min. *Caution: piranha solution is highly corrosive and reacts violently with organic materials. It should be handled with great care.* Upon removal, these cleaned gold slides were rinsed with large amounts of deionized water and ethanol, sonicated in ethanol for 1 h, rinsed with a large amount of ethanol, and then dried in a stream of high-purity nitrogen immediately prior to the formation of thiol monolayers. The procedures for preparing *n*-C<sub>4</sub>H<sub>9</sub>SH-α-CD/CF<sub>3</sub>AzoSH inclusion complexes modified

surfaces were performed as follows, shown in Figure S1. The gold substrates were dipped into the  $1.2 \times 10^{-5}$  M ethanolic solution of  $n\text{-C}_4\text{H}_9\text{SH}$  at room temperature for  $\sim 6$  min and rinsed extensively with ethanol and dried in a stream of dry high-purity nitrogen. Then, the  $n\text{-C}_4\text{H}_9\text{SH}$  modified gold substrates were immersed into the aqueous solution of  $\alpha\text{-CD}/\text{CF}_3\text{AzoSH}$  inclusion complexes ( $C_{\text{CF}_3\text{Azo}}=5 \times 10^{-7}$  M) for  $\sim 8$  min at room temperature and then rinsed with water and dried in a stream of dry high-purity nitrogen before characterization. Other kinds of SAMs were prepared basically following the procedures above. Here, the rough gold substrate used in our experiments is a kind of electrodeposited rough surface, which is well described and characterized in our previous published work.<sup>4</sup>



**Figure S1.** Preparation of mixed SAM of  $n\text{-C}_4\text{H}_9\text{SH}$  and  $\alpha\text{-CD}/\text{CF}_3\text{AzoSH}$  inclusion complexes on rough gold substrate.

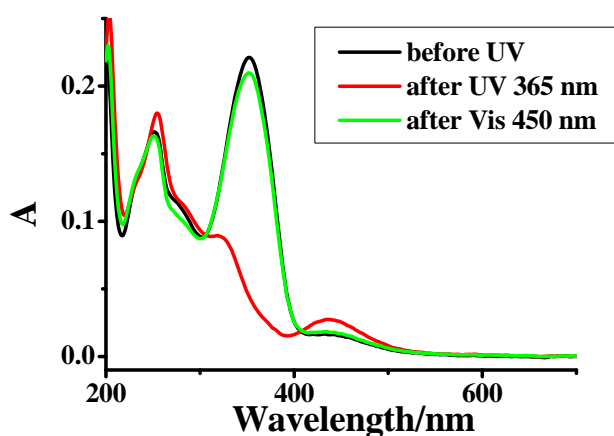
### Experimental for photoisomerization

The irradiation light source for photoisomerization was a high-pressure mercury lamp with an optical fiber (RW-UVA 05-100, purchased from Shenzhen Runwing Mechanical & Electrical Co., Ltd., China), and the intensity was  $900 \text{ mW cm}^{-2}$ . The two band-pass filters were of the wavelengths  $365 \pm 10$  and  $450 \pm 10$  nm, respectively. The irradiation was carried out in an in-situ mode by irradiating the solutions in the UV-vis spectrophotometer with the optical fiber so as to minimize the errors in the experiments. For SAM on gold substrates, the samples were placed about 8~10 cm away from the lamp for 20 min under UV or for 1.5 h under visible light illumination at room temperature. Drops of water were added on surfaces to form the polar conditions when irradiated under visible light for 1.5 h, which is helpful to form  $\alpha\text{-CD}/\text{azobenzene}$  inclusion complexes and influence the surface photoisomerization reaction of azobenzene groups.<sup>5</sup> As reported in this communication, after exposure to UV light (365 nm) for 20 min, the CA change of the  $n\text{-C}_4\text{H}_9\text{SH}\text{-}\alpha\text{-CD}/\text{CF}_3\text{AzoSH}\text{-SAM}$  modified rough surface was found to be about  $50 \pm 2^\circ$ , that is, it was increased from  $70 \pm 2^\circ$  to  $120 \pm 2^\circ$ . Furthermore, when the surface was irradiated with visible light (450 nm) for 1.5 h without drops of water covered on it, the CA was  $132 \pm 2^\circ$ , which responds to the photoisomerization of  $\text{CF}_3\text{AzoSH}$  from the *cis* to the *trans* form but the  $\alpha\text{-CD}$  can not move up because of the interaction between  $\alpha\text{-CD}$  and the alkyl group of  $\text{CF}_3\text{AzoSH}$ . However, when the surface was irradiated with visible light (450 nm) for 1.5 h with drops of water, the CA was restored to its initial

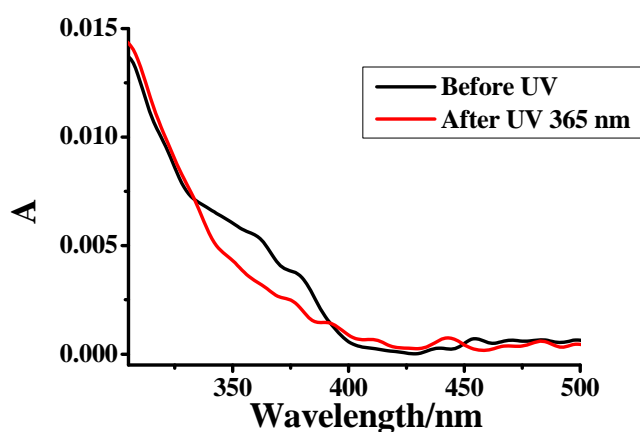
state, which is owing to the photocontrolled down-to-up molecular motion of  $\alpha$ -CD in CF<sub>3</sub>AzoSH-SAMs on gold surfaces leading to the formation of  $\alpha$ -CD/azobenzene inclusion complexes.

### ***Photoisomerization of CF<sub>3</sub>AzoSH and $\alpha$ -CD/CF<sub>3</sub>AzoSH inclusion complexes indicated by UV-vis spectra***

Figure S2 shows the UV-vis spectra of CF<sub>3</sub>AzoSH in ethanol solution ( $C_{CF_3Azo} = 1.4 \times 10^{-5}$  M). Upon irradiation with UV light at 365 nm the absorption band at around 352 nm decreases remarkably, and concomitantly the band at around 437 nm increases slightly. The absorption bands at 352 and 437 nm are ascribed to  $\pi$ - $\pi^*$  and n- $\pi^*$  transitions of the azobenzene, respectively. The change of the absorption bands induced by UV irradiation is indicative of the photoisomerization of CF<sub>3</sub>AzoSH from the *trans* to the *cis* form. When irradiated by visible light at 450 nm, the  $\pi$ - $\pi^*$  absorption increases again with a slight decrease in the n- $\pi^*$  absorption, which indicates that the photoisomerization of CF<sub>3</sub>AzoSH undergoes a change from the *cis* to the *trans* form. From the UV-vis spectra of  $\alpha$ -CD/CF<sub>3</sub>AzoSH inclusion complexes in water ( $C_{CF_3Azo} = 5 \times 10^{-7}$  M) shown in Figure S3, it can be seen basically the same changes at 352 nm and 437 nm upon irradiation with UV and visible light, respectively, which is in good agreement with our previous work.<sup>6</sup>



**Figure S2.** UV-vis absorption spectra of CF<sub>3</sub>AzoSH in ethanol solution ( $C_{CF_3Azo} = 1.4 \times 10^{-5}$  M) before and after UV irradiation.



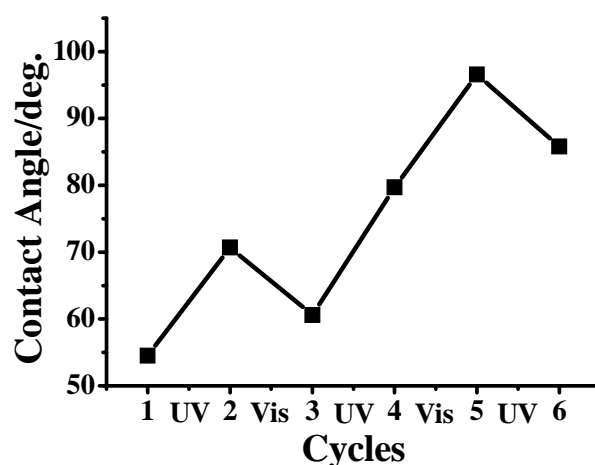
**Figure S3.** UV-vis absorption spectra of  $\alpha$ -CD/CF<sub>3</sub>AzoSH inclusion complexes in water ( $C_{CF_3Azo} = 5 \times 10^{-7}$  M).

### Contact angle measurements

Contact angles were measured at room temperature under ambient conditions using an optical contact angle measuring device (OCA 20, Dataphysics Instruments GmbH) by a sessile drop measuring method, which is a static contact angle assessment. Halogen lighting with continuous adjustable intensity without hysteresis for homogeneous back lighting was used to image the water droplet, whereas a 0.7-4.5-fold magnification CCD-camera video system with a resolution of  $768 \times 576$  pixels was used to monitor and record the data. Ellipse fitting was selected as the default calculation method. The normal test liquid chosen to evaluate the hydrophobicity was deionized water. In each measurement, an about 2  $\mu$ L droplet of water was dispensed onto the substrates under investigation. Contact angles with their error values are given for measurements at five different locations on the gold surfaces modified by different kinds of SAMs set in the *trans* and the *cis* state by irradiation with visible and UV light, respectively.

After the exposure of the Au substrate to UV light for 20 min, the contact angles of the water droplet were recorded, then the substrate was dried carefully in a stream of dry high-purity nitrogen before the next contact angle measurement. Before the exposure of the Au substrate under visible light drops of water were dispensed onto the substrate. After the exposure of such a substrate to visible light for 1.5 h, the substrate was dried carefully in a stream of dry high-purity nitrogen, then the contact angle of the water droplet was recorded.

### CA change of *n*-C<sub>4</sub>H<sub>9</sub>SH- $\alpha$ -CD/AzoSH-SAMs on a rough gold surface



**Figure S4.** CA change of *n*-C<sub>4</sub>H<sub>9</sub>SH- $\alpha$ -CD/AzoSH-SAMs on a rough gold surface upon UV and Vis irradiation.

Figure S4 shows the CA change of *n*-C<sub>4</sub>H<sub>9</sub>SH- $\alpha$ -CD/AzoSH-SAMs on a rough gold surface upon UV and Vis irradiation. The CA change of *n*-C<sub>4</sub>H<sub>9</sub>SH- $\alpha$ -CD/AzoSH-SAMs on a rough gold surface can not be reversible.

## XPS measurements

**Table S1.** XPS peak assignments and atomic composition of *n*-C<sub>4</sub>H<sub>9</sub>SH- $\alpha$ -CD/CF<sub>3</sub>AzoSH-SAMs on gold substrates.

	BE <sup>a</sup>	Obsd atom % <sup>b</sup>	Pred atom % <sup>b</sup>
C1s	284.80	79.33	65.29
N1s	400.00	1.61	1.65
O1s	532.20	17.37	25.62
F1s	688.10	0.50	2.48
S2p	162.05	1.19	4.96
Au4f7/2	83.90		

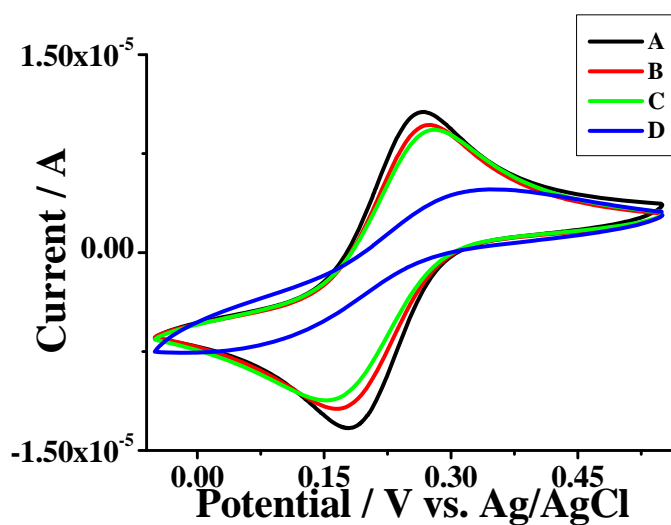
<sup>a</sup> BE=binding energy in eV. <sup>b</sup> Atomic composition in atom %. Abbreviations: obsd atom %= observed atomic composition by XPS; pred atom %=predicted from the molecular formula of the adsorbate molecules (calculated from F 1s).

The XPS spectra were collected with *n*-C<sub>4</sub>H<sub>9</sub>SH- $\alpha$ -CD/CF<sub>3</sub>AzoSH-SAM covered gold substrates as the sample and were calibrated using the binding energy of C 1s as the reference. The binding energy and the elemental composition of the *n*-C<sub>4</sub>H<sub>9</sub>SH- $\alpha$ -CD/CF<sub>3</sub>AzoSH-SAMs are shown in Table S1. From the binding energy and the elemental composition of the mixed SAMs, the ratio of *n*-C<sub>4</sub>H<sub>9</sub>SH and  $\alpha$ -CD/CF<sub>3</sub>AzoSH is estimated to be 5 to 1 (calculated from F 1s) semiquantitatively with an assumption of a 1:1 stoichiometry in  $\alpha$ -CD/CF<sub>3</sub>AzoSH inclusion complexes.

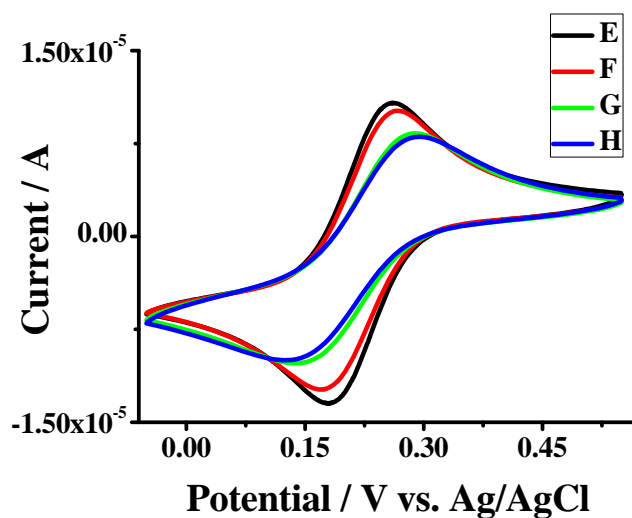
## Experimental for electrochemical measurements

Electrochemical measurement was performed using a potentiostat (Autolab PGSTAT12, Netherlands). It was carried out in a conventional three electrode glass electrochemical cell. A bare gold electrode (model CHI 101, 2 mm diameter) was used as a working electrode. An auxiliary electrode was platinum, and the reference electrode was a Ag/AgCl (saturated KCl) electrode. The experiments were performed at ambient temperature. The gold electrode underwent the following pretreatments to get a mirrorlike surface. First, the gold electrode was mechanically polished with 1  $\mu$ m, 0.3  $\mu$ m, and 0.05  $\mu$ m  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and washed ultrasonically with deionized water. Next, it was electrochemically scanned in a 2 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] + 0.1 M KCl solution by potential scanning between -0.05 and 0.55 V until a reproducible cyclic voltammogram was obtained and then completely rinsed with deionized water and tetrahydrofuran. Finally, it was dried with high-purity nitrogen before monolayer adsorption. The same procedures were used to form the SAMs on gold electrodes as that on gold substrates.

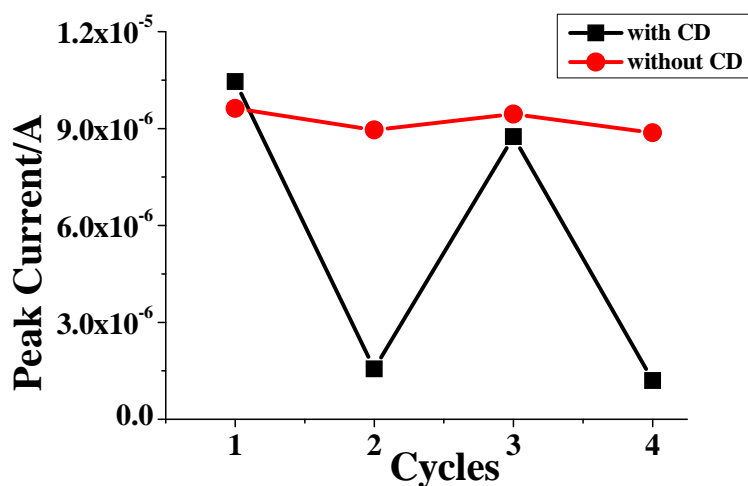
## Ion permeability



**Figure S5.** Cyclic voltammograms of (A) bare gold electrodes, (B)  $n\text{-C}_4\text{H}_9\text{SH-SAM}$  modified gold electrodes, (C)  $n\text{-C}_4\text{H}_9\text{SH-}\alpha\text{-CD/CF}_3\text{AzoSH-SAM}$  modified gold electrodes, (D)  $n\text{-C}_4\text{H}_9\text{SH-}\alpha\text{-CD/CF}_3\text{AzoSH-SAM}$  modified gold electrodes irradiated for 20 min by UV light at 365 nm.

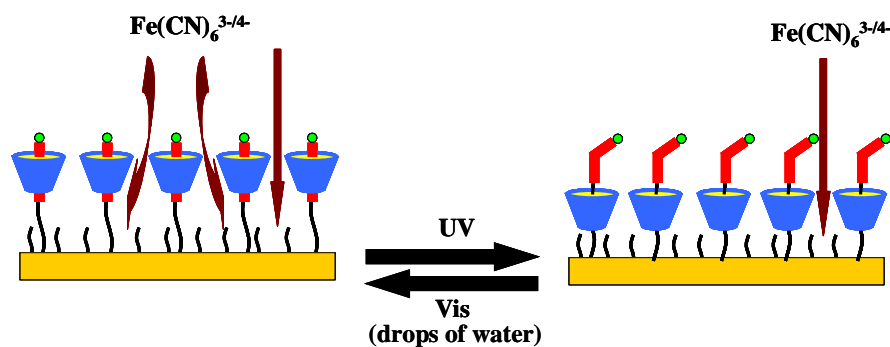


**Figure S6.** Cyclic voltammograms of (E) bare gold electrodes, (F)  $n\text{-C}_4\text{H}_9\text{SH-SAM}$  modified gold electrodes, (G)  $n\text{-C}_4\text{H}_9\text{SH-CF}_3\text{AzoSH-SAM}$  modified gold electrodes, (H)  $n\text{-C}_4\text{H}_9\text{SH-CF}_3\text{AzoSH-SAM}$  modified gold electrodes irradiated for 20 min by UV light at 365 nm.



**Figure S7.** Switching of the peak current upon UV/vis irradiation: ■ peak current on a  $n\text{-C}_4\text{H}_9\text{SH-}\alpha\text{-CD/CF}_3\text{AzoSH-SAM}$  modified gold electrode; ● peak current on a  $n\text{-C}_4\text{H}_9\text{SH-CF}_3\text{AzoSH-SAM}$  modified gold electrode.

To further confirm the photocontrolled molecular motion of  $\alpha\text{-CD/CF}_3\text{AzoSH-SAMs}$  on gold, the cyclic voltammetry (CV) was employed in our experiment using the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  system as a redox probe. Figure S5 shows the cyclic voltammetric responses of the bare (Figure S5 A),  $n\text{-C}_4\text{H}_9\text{SH-SAM}$  (Figure S5 B) and  $n\text{-C}_4\text{H}_9\text{SH-}\alpha\text{-CD/CF}_3\text{AzoSH-SAM}$  (Figure S5 C) modified gold electrodes in the presence of  $\text{Fe}(\text{CN})_6^{3-}$ . In the case of a  $n\text{-C}_4\text{H}_9\text{SH-}\alpha\text{-CD/CF}_3\text{AzoSH-SAM}$  modified gold electrode (Figure S5 C), a pair of easily reversible waves were observed at a scan rate of  $0.10 \text{ V s}^{-1}$ . Figure S5 D shows the cyclic voltammogram of  $n\text{-C}_4\text{H}_9\text{SH-}\alpha\text{-CD/CF}_3\text{AzoSH-SAM}$  modified gold electrodes irradiated for 20 min by UV light at 365 nm. Upon UV irradiation, we observed a quick decrease in the current response, indicating that the SAMs partly inhibit the electron-transfer process between the probe and the gold electrode because of the up-to-down motion of  $\alpha\text{-CD}$ . However, after irradiation with visible light (450 nm) a redox wave of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  was observed (See Figure S7 ■).



**Figure S8.** Chemical representations of ion permeability.



By comparison, we also studied the ion permeability of *n*-C<sub>4</sub>H<sub>9</sub>SH-CF<sub>3</sub>AzoSH-SAM modified gold electrode. Figure S6 shows the cyclic voltammetric responses of the bare (Figure S6 E), *n*-C<sub>4</sub>H<sub>9</sub>SH-SAM (Figure S6 F) and *n*-C<sub>4</sub>H<sub>9</sub>SH-CF<sub>3</sub>AzoSH-SAM (Figure S6 G) modified gold electrodes in the presence of Fe(CN)<sub>6</sub><sup>3-</sup>. Figure S6 H shows the cyclic voltammogram of *n*-C<sub>4</sub>H<sub>9</sub>SH-CF<sub>3</sub>AzoSH-SAM modified gold electrodes irradiated for 20 min by UV light at 365 nm. After irradiation with visible light a redox wave of K<sub>3</sub>[Fe(CN)<sub>6</sub>] was observed (See Figure S7 ●).

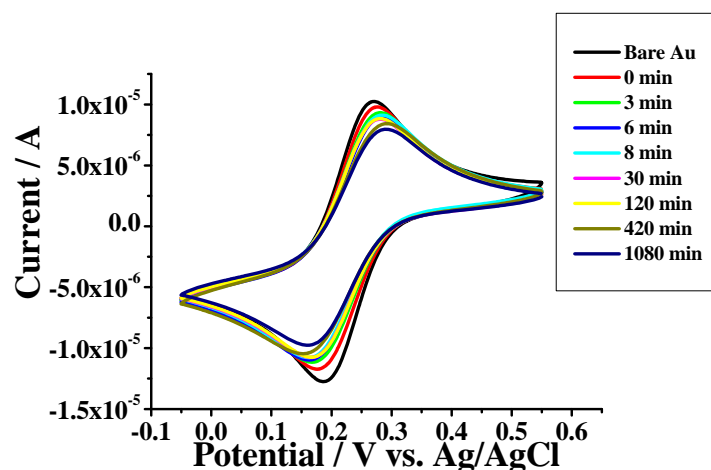
As reported<sup>7</sup>, [Fe(CN)<sub>6</sub>]<sup>3-</sup> is sterically not permeable through the β-cyclodextrin cavity, so the permeability of [Fe(CN)<sub>6</sub>]<sup>3-</sup> through the intermolecular voids should be considered (Figure S8). In the case of a *n*-C<sub>4</sub>H<sub>9</sub>SH-α-CD/CF<sub>3</sub>AzoSH-SAM modified gold electrode (Figure S5 C), that a pair of easily reversible waves were observed at a scan rate of 0.10 V s<sup>-1</sup> is because there are many voids between the intermoleculars of the *n*-C<sub>4</sub>H<sub>9</sub>SH-α-CD/CF<sub>3</sub>AzoSH-SAM modified gold electrode. Upon UV irradiation, we observed a quick decrease in the current response (Figure S5 D), indicating that the SAMs partly inhibit the electron-transfer process between the probe and the gold electrode because of the less intermolecular voids from the up-to-down motion of α-CD. However, the permeability barrier (Figure S6) of *n*-C<sub>4</sub>H<sub>9</sub>SH-CF<sub>3</sub>AzoSH-SAM modified gold electrode from the *trans* to *cis* photoisomerization of the azobenzene via UV irradiation was very little compared to that from the up-to-down motion of α-CD. Therefore, the CV data confirm the photocontrolled up-down motion of α-CD in CF<sub>3</sub>AzoSH-SAMs on gold surfaces.

#### ***Optimized conditions of SAM with various immersion time***

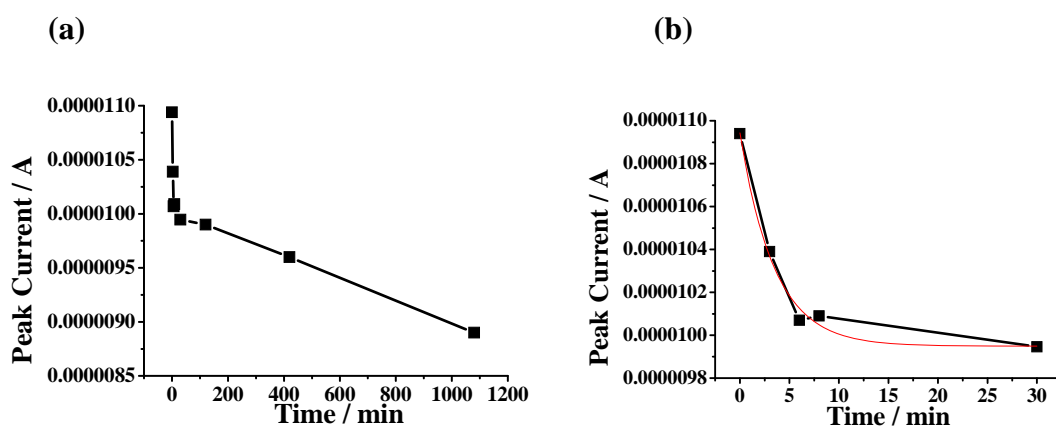
In our experiment, the rough gold substrate was obtained by engaging static potential gold electrodeposition on a flat gold substrate at -200 mV (vs Ag/AgCl) in a HAuCl<sub>4</sub>/ H<sub>2</sub>SO<sub>4</sub> mixed electrolyte solution for 3200 s. However, the rough gold substrates we obtained were superhydrophilic surfaces. After being modified with SAM of α-CD/CF<sub>3</sub>AzoSH inclusion complexes, the rough surface was still superhydrophilic and without any change under UV irradiation. This phenomenon may be due to the dense SAM of α-CD/CF<sub>3</sub>AzoSH inclusion complexes to inhibit the movement of the molecular shuttle or the superhydrophilic surface from the rough surface amplification. Therefore, a dilute SAM of *n*-C<sub>4</sub>H<sub>9</sub>SH was employed to form mixed SAMs with α-CD/CF<sub>3</sub>AzoSH inclusion complexes. Table S2 gives contact angles of the rough surface at different immersion time in *n*-C<sub>4</sub>H<sub>9</sub>SH solution (1.2 × 10<sup>-5</sup> M). We found that it took ~ 6 min to get more hydrophobic (66.9°) compared to the superhydrophilic rough surface without any modification. At this immersion time, the CA change of the mixed SAM of *n*-C<sub>4</sub>H<sub>9</sub>SH and α-CD/CF<sub>3</sub>AzoSH inclusion complexes is so large, almost 50°. It is assumed that at this immersion time, more free volumes are provided for the photoisomerization of CF<sub>3</sub>AzoSH from the *cis* to the *trans* form and the photocontrolled up-down motion of α-CD in CF<sub>3</sub>AzoSH-SAMs on gold substrates upon UV/vis irradiation. So we chose the immersion time in *n*-C<sub>4</sub>H<sub>9</sub>SH solution ~6 min in our experiment.

**Table S2.** Contact angles of the rough surface (electrodeposition time 3200 s) after being modified with a  $n\text{-C}_4\text{H}_9\text{SH}$  solution ( $1.2 \times 10^{-5}$  M) at different immersion time.

Time/s	5	15	50	110	180	240	300	360	480
CA/deg.	7.4	17.2	25.3	35.5	47.7	51.0	61.2	66.9	93.4



**Figure S9.** Cyclic voltammograms of  $n\text{-C}_4\text{H}_9\text{SH}\text{-}\alpha\text{-CD/CF}_3\text{AzoSH-SAM}$  modified gold electrodes at different immersion time in  $\alpha\text{-CD/CF}_3\text{AzoSH}$  inclusion complex solution ( $C_{\text{CF}_3\text{Azo}}=5 \times 10^{-7}$  M).



**Figure S10.** The peak currents of the cyclic voltammograms of Figure S9 at different immersion time in  $\alpha\text{-CD/CF}_3\text{AzoSH}$  inclusion complex solution. a): from 0 h to 18 h ; b): from 0 min to 30 min.

Figure S9 demonstrates the cyclic voltammograms of  $n\text{-C}_4\text{H}_9\text{SH}\text{-}\alpha\text{-CD/CF}_3\text{AzoSH-SAM}$  modified gold electrodes at different immersion time in  $\alpha\text{-CD/CF}_3\text{AzoSH}$  inclusion complex solution. Figure S10 shows the peak currents of the cyclic voltammograms of Figure S9 at different immersion time in  $\alpha\text{-CD/CF}_3\text{AzoSH}$  inclusion complex solution. From Figure S10-b, we can see the decrease rate of the peak current before 8 min is higher than that after 8 min as the immersion time goes on. Because free spaces may be needed in the *trans* to *cis* photoisomerization of the azobenzene and the photocontrolled up-down motion of  $\alpha\text{-CD}$  in  $\text{CF}_3\text{AzoSH-SAMs}$  on gold substrates upon UV/vis irradiation,<sup>8</sup> we chose  $\sim 8$  min as

the immersion time in  $\alpha$ -CD/CF<sub>3</sub>AzoSH inclusion complex solution in our experiment to form the low density self-assembly monolayer.

## References:

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