Host-guest chemistry at interface for photoswitchable bioelectrocatalysis

Pengbo Wan,[a] Yibo Xing,[a] Yueyue Chen,[b] Lifeng Chi[b] and Xi Zhang*[a]

[a] *Key Lab of Organic Optoelectronics & Molecular Engineering,*
Department of Chemistry, Tsinghua University, Haidian District,
Beijing 100084, China. Fax: +86-10-62771149; Tel: +86-10-62796283;
E-mail: xi@mail.tsinghua.edu.cn

[b] *Physikalisches Institut, Westfälische Wilhelms-Universität, Münster 48149, Germany.*

***Materials**:* AzoSH was synthesized previously.[1] PAA_{319}-g-$CD_{18\%}$ was prepared according to previous literature.[2] The ratio of grafting was estimated from ^{1}HNMR. GOx (EC 1.1.3.4; type X-S from Aspergillus niger), 1-decanethiol (96%), ferrocenemethanol and glucose were purchased from Sigma-Aldrich and used without further purification. All solutions were prepared by using Milli-Q purified water (>18.0 MΩ cm) that had been sterilized at high temperature.

***Electrochemical Measurements**:* Electrochemical measurement was performed using a potentiostat (Autolab PGSTAT12, the Netherlands). It was carried out in a conventional three-electrode glass electrochemical cell at ambient temperature. 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 an Ag/AgCl (saturated KCl) electrode. The gold electrode underwent the following pretreatments to get a mirror-like surface. First, the gold electrode was mechanically polished with 1 μm, 0.3 μm, and 0.05 μm α-Al_2O_3 and washed ultrasonically with deionized water. Next, it was electrochemically scanned in a 2 mM $K_3[Fe(CN)_6]$ + 0.1 M KCl solution (pH 6.2) 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 solutions for the electrochemical measurements were purged prior to the measurements by continuously bubbling highly purified nitrogen through them for 30 min, and a nitrogen atmosphere environment was maintained during the electrochemical measurements. The Azo SAM was formed by placing the bare gold electrode in a 10^{-5} M ethanolic solution of n-$C_{10}H_{21}SH$ and AzoSH (10:1, molar ratio) at room temperature for 90 min and then rinsed extensively with ethanol and dried in a stream of dry high-purity nitrogen. The PAA-g-CD attached Azo SAM was fabricated by dipping the Azo SAM modified gold electrode into a 0.2 mg mL^{-1} aqueous solution of PAA-g-CD at room temperature overnight.[3] After immersion into 0.5 mg mL^{-1} ferrocenemethanol solution (water : ethanol, v/v=3:1) at room temperature overnight, ferrocenemethanols are bound into the empty CDs of PAA-g-CD/Azo SAM modified electrode because of the host-guest interaction of Fc and CD.

The surface coverage of bound Fc in free CDs of PAA-g-CD/Azo SAM modified Au electrode was calculated according to Laviron's equation with a roughness factor of 1.5 at a scan rate of 50 mV s^{-1}.[4] The electron transfer rate constant (k_s) of bound Fc in free CDs of PAA-g-CD/Azo SAM modified Au electrode was calculated according to the equation below,[5] taking a charge transfer coefficient α of 0.5, and a scan rate of 50 mV s^{-1}.

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log\frac{RT}{nF\nu} - \frac{\alpha(1-\alpha)nF\Delta E_p}{2.3RT}$$

Light Irradiation: 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 mW cm^{-2}. The two bandpass filters with about 35% of light transmission ratio were of the wavelengths 365 ± 10 and 450 ± 10 nm, which can be used to produce the UV light with wavelength at 365 nm and visible light with wavelength at 450 nm, respectively. The various modified gold substrates were placed about ~8 cm away from the lamp in an aqueous environment for 35 min under

UV or for 50 min under visible light illumination at room temperature to eliminate the influence of heat.

CV Formal Potential of Fc in Solution and Immobilized on Surface

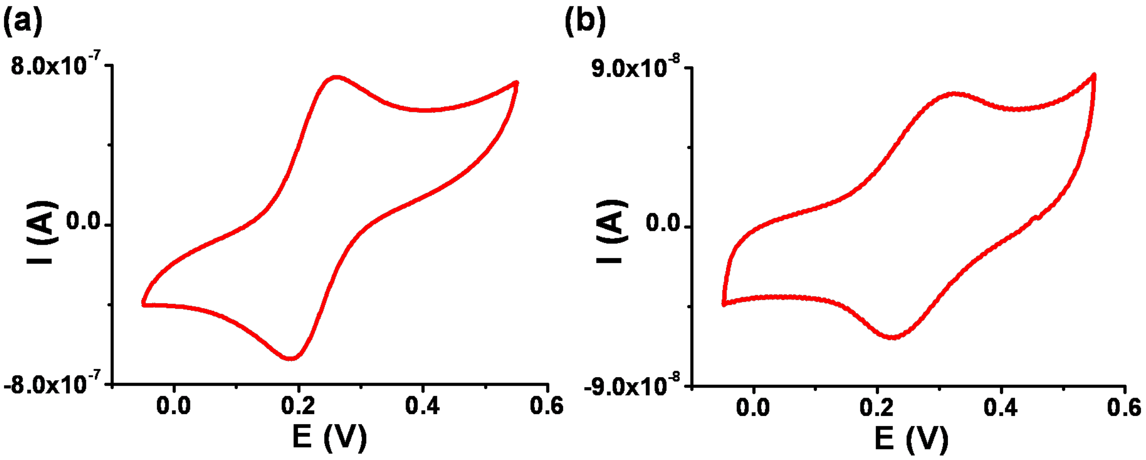

Fig. S1 (a) Characteristic CV responses of Fc in solution (Bare Au in 0.1 M Na_2SO_4 + 10 mM PBS pH 7.0 + 0.05 mg mL^{-1} Fc at the scan rate of 25 mV s^{-1}) and (b) bound into the free CDs of PAA-g-CD on surfaces (PAA-g-CD-Fc/Azo SAM modified electrodes in 0.1 M Na_2SO_4 + 10 mM PBS pH 7.0 at the scan rate of 25 mV s^{-1}).

In comparison with characteristic CV formal potential of Fc (0.21 V) in solution, CV formal potential of bound Fc (0.28 V) shifts positively, indicating that Fc is bound into the empty CDs of PAA-g-CD on surfaces from the formation of complex between Fc and CD.[6]

XPS Measurement for Azo SAM

Table S1 Atomic composition of Azo SAM on gold substrates from XPS measurement. The ratio of *n*-$C_{10}H_{21}SH$ and AzoSH is about 9 to 1 (approximately estimated from C 1s and N 1s).

	Obsd atom %
C 1s	55.36
N 1s	0.58
O 1s	16.01
S 2p	1.08
Au 4f	26.96

Atomic composition in atom %. Abbreviation: obsd atom %=observed atomic composition by XPS.

X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantera SXM spectrometer with an AlKa X-ray source. The base pressure in the XPS analysis chamber during spectral acquisition was 6.7×10^{-8} Pa. The spectra were collected with the Azo SAMcovered gold slides as the sample substrate and were calibrated using the binding energy of C 1 s as the reference.

Optimized Component Ratio of Mixed SAMs

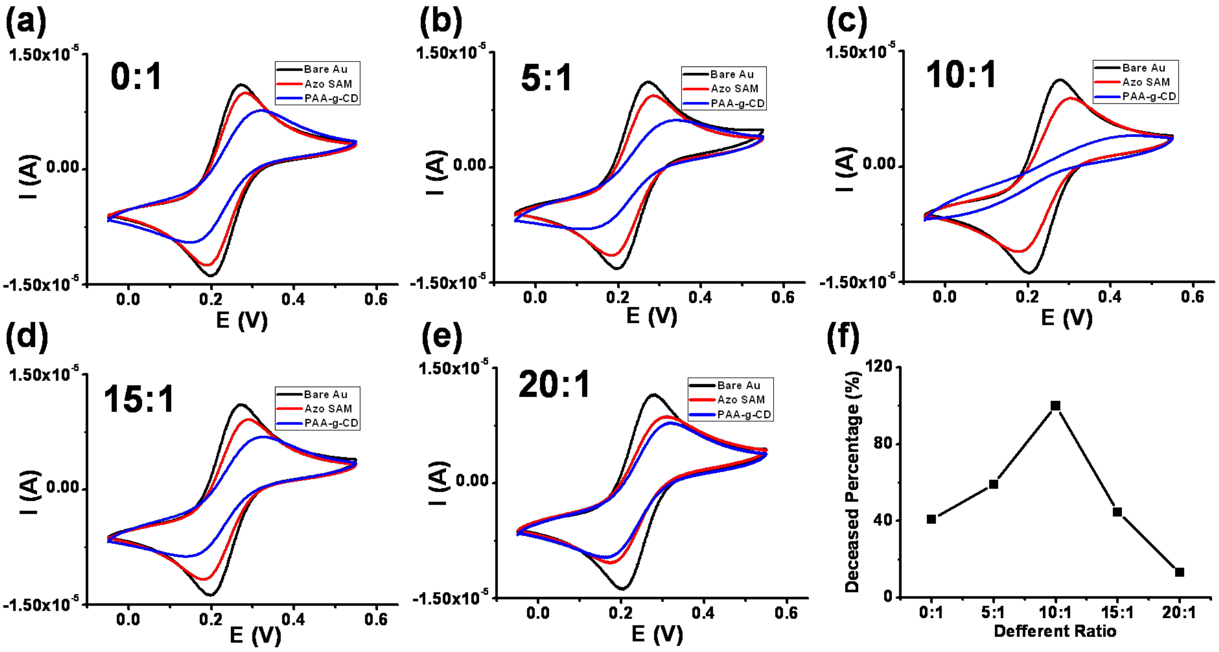

Fig. S2 CV responses for PAA-g-CD/Azo SAM modified electrodes from different ratios of mixed SAMs (the ratio of *n*-$C_{10}H_{21}SH$ and AzoSH at (a) 0:1, (b) 5:1, (c) 10:1, (d) 15:1, (e) 20:1, black curve-bare Au, red curve-Azo-SAM, blue curve-PAA-g-CD) in 2 mM $K_3[Fe(CN)_6]$ + 0.1 M KCl solution at a scan rate of 100 mV s^{-1}. (f) After immobilization of PAA-g-CD, the percentage of deceased CV response using the deceased percentage of (c) as the standard.

Fig. S2 shows the CV responses for PAA-g-CD/Azo SAM modified electrodes from different ratios of mixed SAMs (the ratio of *n*-$C_{10}H_{21}SH$ and AzoSH at (a) 0:1, (b) 5:1, (c) 10:1, (d) 15:1, (e) 20:1, black curve-bare Au, red curve-Azo-SAM, blue curve-PAA-g-CD). After immobilization of PAA-g-CD, the percentages of deceased CV responses using the deceased percentage of (c) as the standard are shown in Fig. S2 (f). As indicated from Fig. S2 (f), the mixed SAM at the ratio of 10:1 for *n*-$C_{10}H_{21}SH$ and AzoSH can immobilize more PAA-g-CD.

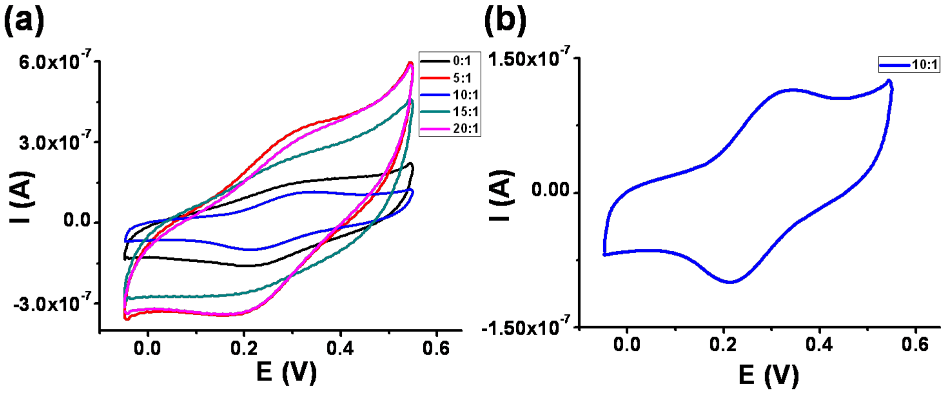

Fig. S3 (a) CV responses of Fc for PAA-g-CD-Fc/Azo SAM modified electrodes from different ratios of mixed SAMs in 0.1 M Na_2SO_4 + 10 mM PBS pH 7.0 at the scan rate of 50 mV s^{-1}. (b) The CV response of Fc for PAA-g-CD-Fc/Azo SAM modified electrode from the ratio of mixed SAM at 10:1.

Fig. S3 shows the CV responses of Fc for PAA-g-CD-Fc/Azo SAM modified electrodes from different ratios of mixed SAMs in 0.1 M Na_2SO_4 + 10 mM PBS pH 7.0 at the scan rate of 50 mV s^{-1}. As implied from Fig. S3 (a) and (b), the PAA-g-CD/Azo SAM modified electrode from the ratio of mixed SAM at 10:1 can bind more Fc in the free CDs of PAA-g-CD.

Optimized n-$C_nH_{2n+1}SH$ Length for Mixed SAMs

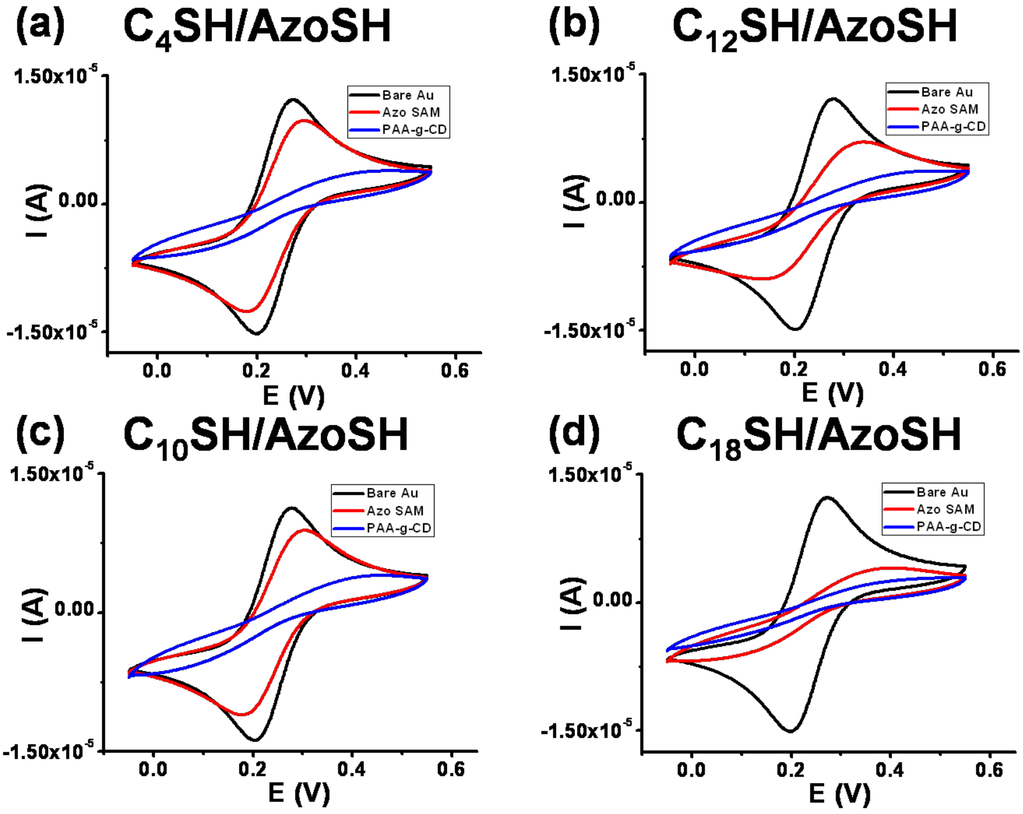

Fig. S4 CV responses for PAA-g-CD/Azo SAM modified electrodes from different *n*-$C_nH_{2n+1}SH$ length of mixed SAMs in 2 mM $K_3[Fe(CN)_6]$ + 0.1 M KCl solution at a scan rate of 100 mV s^{-1}.

Fig. S4 shows the CV responses for PAA-g-CD/Azo SAM modified electrodes from different *n*-$C_nH_{2n+1}SH$ length of mixed SAMs. As demonstrated from Fig. S4, the conductivity of the PAA-g-CD/Azo SAM modified electrode from *n*-$C_{18}H_{37}SH$ of mixed SAM is not that good.

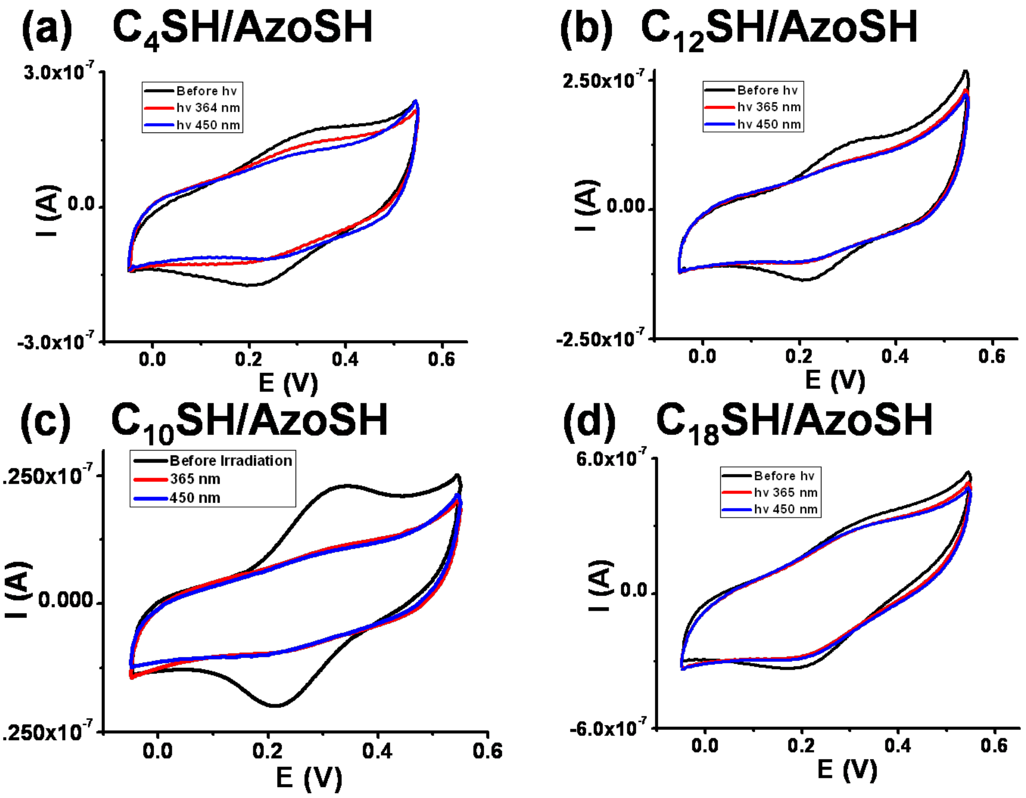

Fig. S5 CV responses of Fc for PAA-g-CD-Fc/Azo SAM modified electrodes from different *n*-$C_nH_{2n+1}SH$ length of mixed SAMs in 0.1 M Na_2SO_4 + 10 mM PBS pH 7.0 at the scan rate of 50 mV s^{-1}.

Fig. S5 shows the CV responses of Fc for PAA-g-CD-Fc/Azo SAM modified electrodes from different *n*-$C_nH_{2n+1}SH$ length of mixed SAMs in 0.1 M Na_2SO_4 + 10 mM PBS pH 7.0 at the scan rate of 50 mV s^{-1}. As implied from Fig. S5, the PAA-g-CD/Azo SAM modified electrode from *n*-$C_{10}H_{21}SH$ of mixed SAM can bind more Fc in the free CDs of PAA-g-CD. Meanwhile, the PAA-g-CD/Azo SAM modified electrode from *n*-$C_{10}H_{21}SH$ of mixed SAM can be even better for the reversible immoblization and release of PAA-g-CD-Fc.

Scan Rate Dependence of Fc in PAA-g-CD-Fc/Azo SAM Modified Electrode

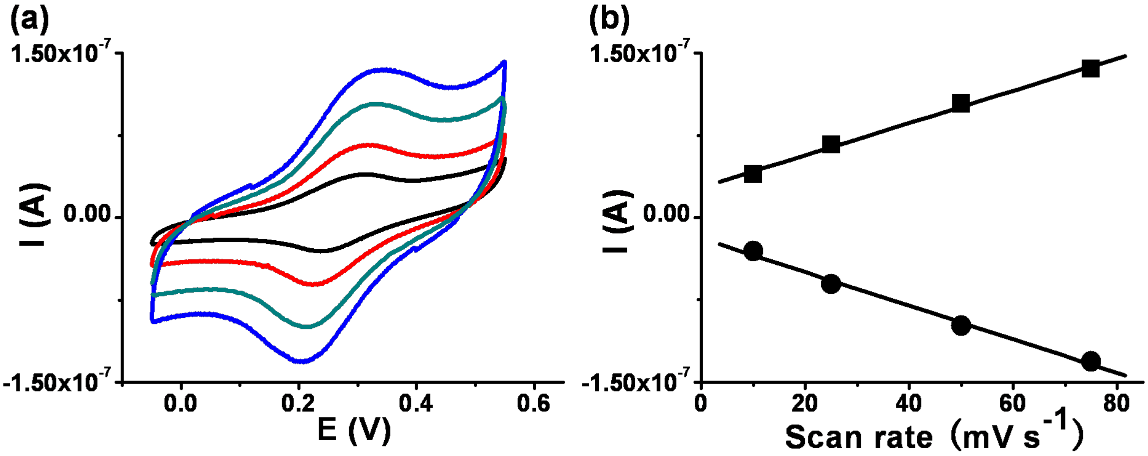

Fig. S6 (a) Cyclic voltammograms of Fc in PAA-g-CD-Fc/Azo SAM modified electrode performed in 0.1 M Na_2SO_4 + 10 mM PBS pH 7.0 at scan rates of 10 mV s^{-1}, 25 mV s^{-1}, 50 mV s^{-1}, 75 mV s^{-1}. (b) Plots of cathodic and anodic peak currents versus the scan rates.

Fig. S6 shows the scan rate dependence of Fc in PAA-g-CD-Fc/Azo SAM modified electrode. Both the anodic and cathodic peak currents vary linearly with the scan rates in the range of 10-75 mV s^{-1}, indicative of a surface-controlled process of Fc in PAA-g-CD-Fc/Azo SAM modified electrode.

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