Support information:

1. Fc-DNA synthesis, Fc-DNA, Fc-DNA-SS-C_3
2. HPLC purification
3. UV, MS characterization
4. XPS characterization for the monolayer on gold surface.

1. Chemicals and reagents

Ferrocene carboxylic acid (Fluka) 1-hydroxy-1H-benzotriazole (Fluka) and 1-ethyl-3(3-dimethylaminopropyl), carbodiimide (EDC, Merck) were purchased and used without further purification. Other chemicals are analytical grade. All solutions were prepared in Millipore filtered water.

The DNA (20 mer) sequences used in this study are shown below:

5'-NH_2-$(CH_2)_3$-AAC TAC TGG GCC ATC GTG AC-$(CH_2)_3$-S-S-3'

5'-GTC ACG ATG GCC CAG TAG TT-$(CH_2)_3$-NH_2-3'

5'-AAC TAC TGG GCC ATC GTG AC-$(CH_2)_3$-S-S-3'

5'-GTC ACG ATA ACC CAG TAG TT-3'

All DNA samples were synthesized by the DNA automatic standard solid phase synthesizer and characterized by matrix-assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF MS).

2. Synthesis

2.1. Fc-OBt

To a solution of 0.5 g (2.1 mmol) ferrocene carboxylic acid (Aldrich) in 20 ml CH_2Cl_2, 0.3 g (2 .1 mmol) 1-hydroxy-1H-benzotriazole (HOBT, Merck) were added and stirred. After cooling to 0 C, 0.4 g (2.1 mmol) solid 1-ethyl-3(3-dimethylaminopropyl)cabodiimide (EDC, Merck) was added.

2.2. Fc-DNA

DNA-NH_2 (82 g, 40 nmol) was dissolved in 0.5 ml $NaCO_3$-$NaHCO_3$ buffer solution (pH=9) and added to a solution of Fc-OBt (0.2 mg, 0.6 mol) dissolved in 0.1 ml of THF and stirred overnight. The ferrocenoyl-DNA crude product was purified by RP-HPLC and then analyses by MALDI-TOF mass spectroscopy. The yield was 76%.

3. Electrochemistry

3.1. Preparation of gold microelectrodes

Gold wire, diameter, 50 m, melting fixed in soft glass, polishing with a 0.05 m alumina slurry, cleaned by soaking in hot Piranha solution (H_2SO_4:H_2O_2=3:1), 10 min. (***Caution!*** *Piranha solution should be handled with extreme care and should never be stored in a closed container. It is a very strong oxidant and reacts violently with most organic materials.*) and then sonicated in Millipore H_2O, twice. After careful characterization of the microelectrode as a defined disk shape and smooth surface under microscopy, it was electrochemically cycled from a potential of –0.1 to +1.25 V vs. Ag/AgCl in 0.5 M H_2SO_4 solution until a stable gold oxidation peak at 1.1 V vs. Ag/AgCl was observed.

3.2 Preparation of DNA modified gold electrodes

Incubate the microelectrodes in 0.05 mM double strands DNA, 20 mM Tris-ClO_4 buffer solution (pH=8.68) for 5 days. The electrodes were rinsed with Tris-ClO_4 buffer and mounted into an electrochemical cell.

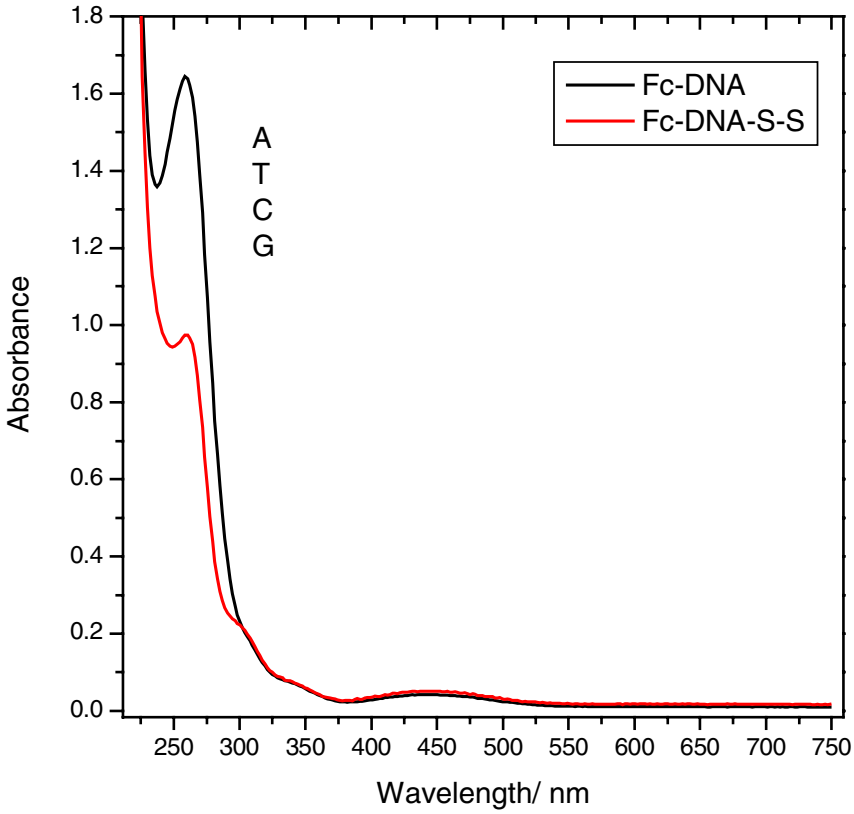
3.3 Electrochemical measurement

Electrochemical measurements were performed using a custom-built electrochemical system for microelectrode. The gold microelectrode (50 μm diameter) serves as a working electrode. The cell was enclosed in a grounded Faraday cage. A reference electrode was constructed by sealing Ag/AgCl wire into a glass tube with a solution of 3M KCl capped with a Vycor tip. The reference electrode was always isolated from the cell by a Luggin capillary containing the electrolyte. The salt-bridge reference electrode was used because of limiting Cl^- ion leakage for the normal Ag/AgCl reference electrode to

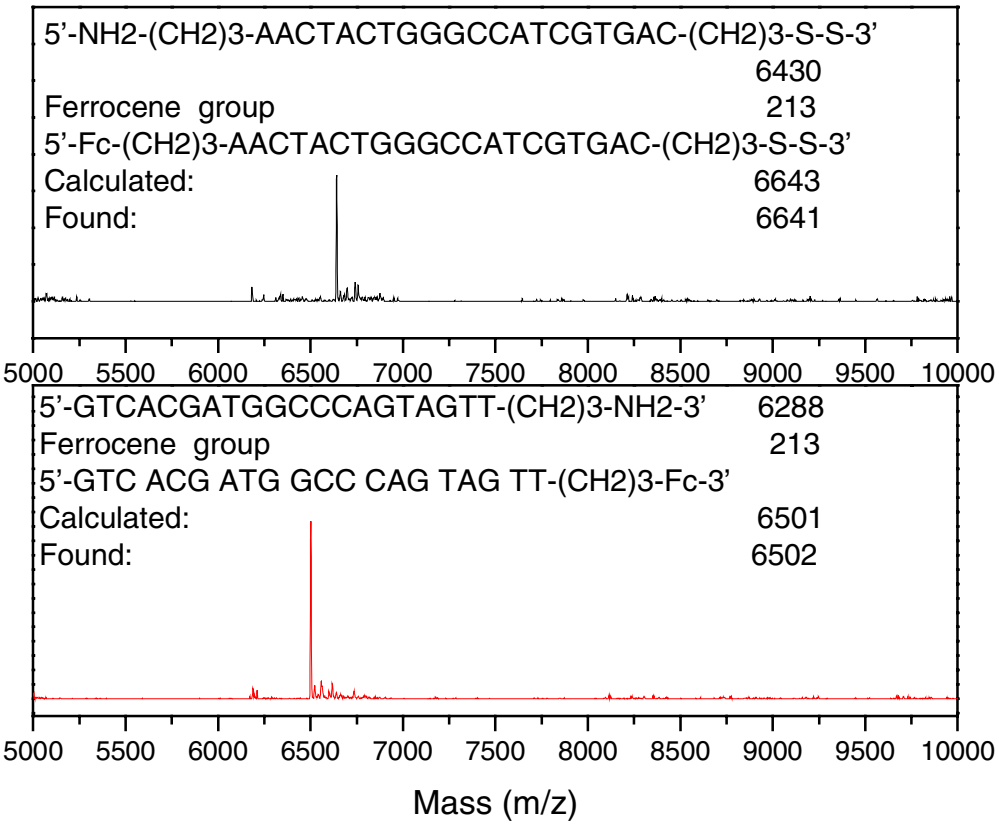
the measurement system. The counter electrode was a platinum wire. All electrolyte solutions were purged for a minimum of 20 min. in Ar prior to the measurements, and a blanket of Ar was maintained over the solutions during the measurements. All experiments were conducted at room temperature (22 3 C).

4 X-ray photoelectron spectroscopy (XPS).

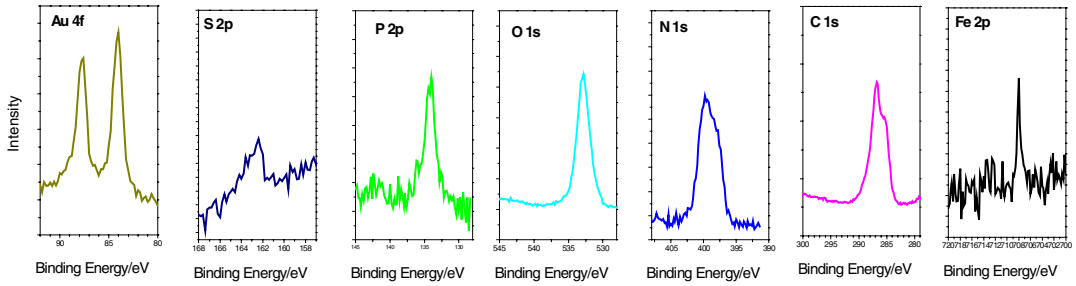
Leybold MAX200 photoelectron spectrometer equipped with an Al K radiation source (1486.6eV) was used for collecting electron photoemission spectra. The base pressure during measurements was maintained less than 10^{-9} mbar in the test chamber. The takeoff angle was set at 60^0, and the routine instrument calibration standard was taken to be the Au $4f_{7/2}$ peak (binding energy 84.1eV). The pass energy of the energy analyzer was set to 48eV and 96eV for the survey and core scans, respectively. The XPS samples are prepared on Au-coated mica (deposited 100nm gold on mica).



UV-visible Absorption spectra of Fc-DNA and Fc-DNA



Mass spectra of Fc-DNA (I) and Fc-DNA (II).



X-ray photoelectron spectra of the DNA on gold surface.