Supporting Information

Design of Switchable Wettability sensor for Paraquat based on Clicking Calix[4]arene

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1. Instruments and Materials.

Instruments.

The static water contact angle was measured at 25 °C by means of an OCA 20 contact angle system (Dataphysics, Germany). Electrochemical measurements were performed on CHI-660C workstation (Shanghai, China) with a conventional three-electrode system. X-ray photoelectron spectroscopy (XPS) was gained by PHI Quantera SXM. Scanning electron microscopy (SEM) was recorded by a Hitachi S-4700 electron microscope.

Materials.

C4AE, TLAD and the four guests were synthesized according to references. Silicon wafer was purchased from Silicon Materials Corporation (Germany), using laser to etch it into micro-nano structure surface and then spraying a thin gold layer to its surface. Mill-Q water was used to prepare all solutions in this study.

2. Experiments.

2.1 Preparation of C4AE modified gold surfaces.

Preparation of C4LA modified gold electrode. Au electrode was polished with alumina powder slurry (0.3 down to 0.05 μm, Buehler) and rinsed with water, ethanol and then water for 3 min, respectively. Then, the substrate gold electrode was soaked in piranha solution (H_2SO_4: 30% H_2O_2 = 3:1) for 30 min to eliminate the adsorbed organic substances and then rinsed with water. Finally, it was sonicated for 5 min in ethanol and water, respectively. The clean electrode was dried under argon. The electrode was cycled between 0 and +1.5 V at 100 $mV \cdot s^{-1}$ in 0.5 M H_2SO_4 solution until a stable cyclic voltammogram was obtained. The obtained activated gold electrode can be used in the following experiments. SAMs of TLAD (TLAD SAMs) were prepared by dipping the gold beads into (1.0×10^{-3} M) for 24 h in CH_3CN. And SAMs of calix[4]arene acetylene (C4AE SAMs) were obtained by click chemistry. The TLAD SAMs, which was washed by acetonitrile and then dried by nitrogen to excepting the free TLAD molecules, immerged into the solution containing 5 mM Cu^+ and 1 mM C4AE dimethylformamide (DMF) solution for 24 h. The treated gold beads were immerged into DMF for 10 min to wash off the free C4AE on the surface and then dried under a stream of N_2 and at last C4AE SAMs were obtained.

According to the same method and processes of constructing C4AE SAMs, C4AE modified gold film surfaces including the smooth and micro-nano surfaces were obtained again. At first, the gold surfaces immerge into acetone for 6 h in order to remove organic impurities pollutants and then the gold surfaces were respectively washed by ehtanol and water for three times until the gold surfaces completely cleaned. At last, the C4AE SAMs synthesis processes are the same as the C4AE SAMs electrode surfaces.

2.2 Wettability selectively recognition for paraquat on micro−nano gold surface.

The wettability property (the CA values all refer to static CAs) was performed with a water droplet (1.000 μL) and side-view photographs were obtained after 5 second of adding the water droplet. The successfully modified gold surface of C4AE was firstly performed by contact angle as control experiment. C4AE SAMs were dipped into solutions containing the four recognizing guests (0.05 mL, 1.0 mM) for 5 min, respectively and then were flushed by a little water (0.15 ± 0.05 mL), dried by nitrogen and then measured.

2.3 Impedance selectivity for paraquat.

Impedance spectroscopy (EIS) was performed on a conventional three-electrode system with platinum wire as auxiliary electrode, saturated calomel electrode (SCE) as reference and the treated gold electrode as the working electrode in a one-compartment three-electrode cell. The impedance spectra were recorded over the frequency range of 1−100000 Hz, a potential of +0.200 V and excitation amplitude at 10 mV (rms). The impedance experiments were carried: hexacyanoferrate (II)/(III) (5.0 mM) as redox probe, KNO_3 (100 mM) as electrolyte in aqueous solution at room temperature and the four guests (0.10 mM) being in solutions respectively.

2.4 Anti-interference experiments for paraquat.

Firstly, C4AE SAMs were dipped into the solution of paraquat (0.05 mL, 1.0 mM) for 5 min, and then were flushed by little water, dried by nitrogen. Secondly, the solutions of compound **a**, **c** and **d** (0.05 mL, 1.0 mM)were added onto the dealed surface for 5 min, respectively, and then were flushed by little water, dried by nitrogen and then measured.

2.5 Effect of pH on recognition of paraquat characterized by contact angle.

Phosphate buffer solution with pH range is from 1.0 to 14.0 have been prepared and paraquat solutions in different pH (1.0×10^{-3} M) were formulated. Then according to experimental steps of measuring contact angle, effect of pH on recognition of paraquat characterized by contact angle was investigated.

2.6 Synthesis of **c** compound.

4-(pyridin-4-yl)pyridine (0.156 g, 1 mmol) was dissolved in dry 2,5-dimethylfuran (2 ml). Then 4-bromobut-1-ene (0.54 g, 4 mmol) was added to and the mixture was stirred for 2 h at room temperature. After then the reaction mixture was filtered, the filtrate was washed with ether. The obtained product is solid. ^{1}H NMR (600 MHz, D_2O) δ 9.57 – 9.18 (m, 4H, ArH), 9.06 – 8.55 (m, 4H, ArH), 6.36 (d, *J* = 11.6, 5.1 Hz, 2H, -CH=), 5.74 (dd, *J* = 24.4, 14.8 Hz, 4H, C=CH_2), 5.63 – 5.32 (m, 4H, NCH_2); ^{13}C NMR (150 MHz, D_2O) δ 152.87 (s, ArC), 148.73–143.91 (m, ArC), 132.25 (s, -CH=), 129.63 (d, ArC), 126.66 (s, CH_2=), 66.30 (s, NCH_2).

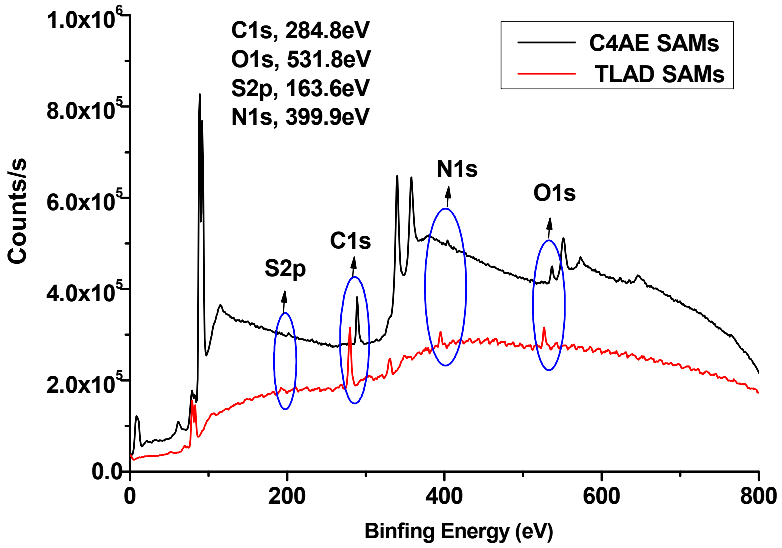


Figure S1. X−ray photoelectron spectroscopy (XPS) of C4AE and TLAD modified on surface.

Table 1. Elements of the composition and content for C4AE and TLAD modified on surface characterized by XPS.

Element (%)	C	O	N	S
C4AE	69.72	11.21	6.36	6.72
TLAD	34.47	9.72	32.69	20.26

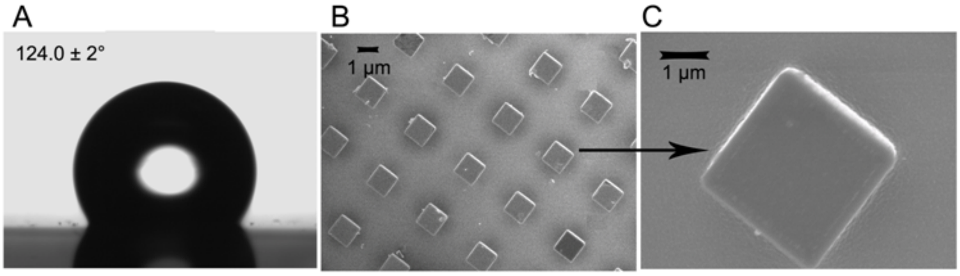


Figure S2. (A) Water-drop profiles on micro-nano gold surface (bare gold surface); (B) Scanning electron microscope image (SEM) of the micro-nano surface; (C) The detail morphology in B.

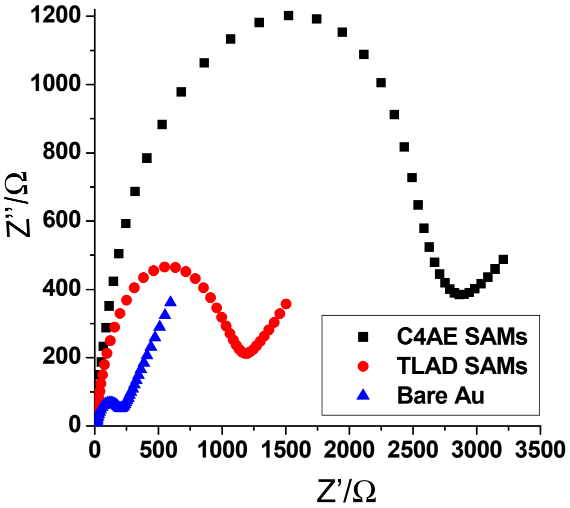


Figure S3. Impedance values (R_{ct}) of 5.0 mM $Fe(CN)_6^{3-/4-}$ in 0.10 M KNO_3 aqueous solution on bare gold surface, TLAD SAMs and C4AE SAMs electrode with the frequency ranging from 100 KHz to 1.0 Hz , scan rate: 0.10 v/s, indicating that C4AE successfully modified on gold surface by clicking reaction in situ.

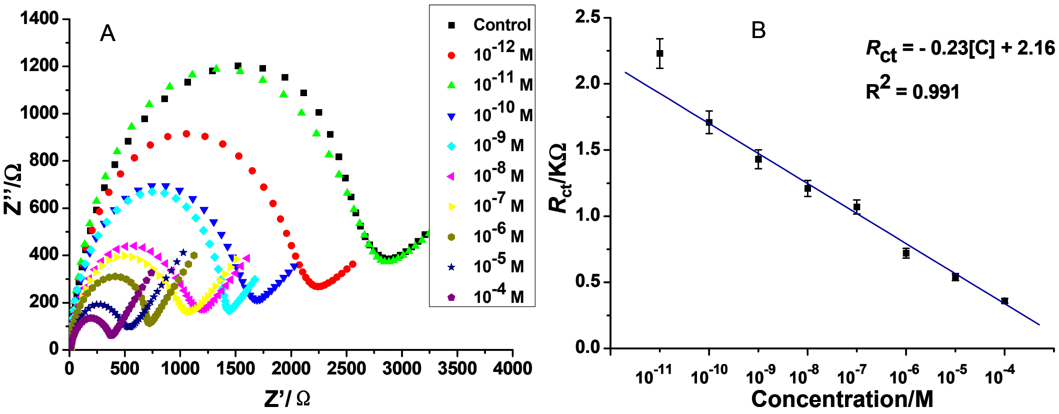


Figure S4. A) Impedance spectroscopy of $Fe(CN)_6^{3-/4-}$ as redox probe in the presence of increasing concentrations of paraquat (1.0×10^{-12} – 1.0×10^{-4} M); B) a plot of the R_{ct} versus concentrations of paraquat (1.0×10^{-11} – 1.0×10^{-4} M), indicating that R_{ct} value is good linear relationship with the increasing concentration of paraquat.

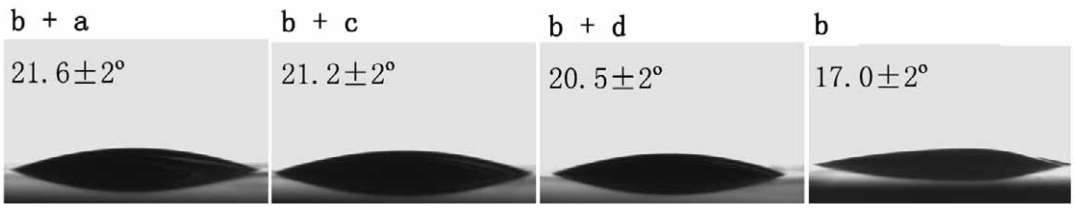


Figure S5. CA relationship images of C4AE SAMs responsing to paraquat in presence and absence of solutions of compound **a**, **c** and **d**, respectively. The result of experiments indicates that the guests of **a**, **c** and **d** can not obviously affect contact angle of C4AE SAMs when it exposes into the solution of **b** compound.

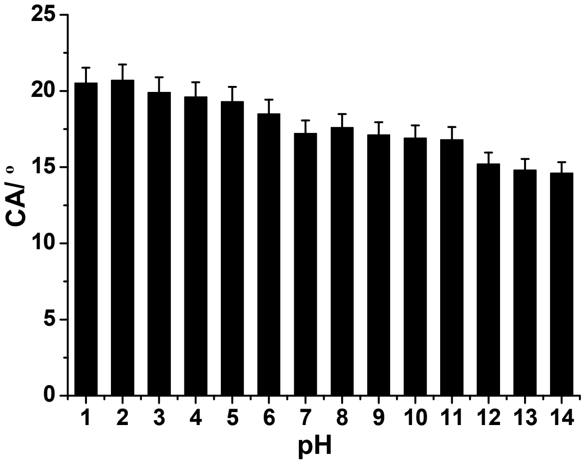
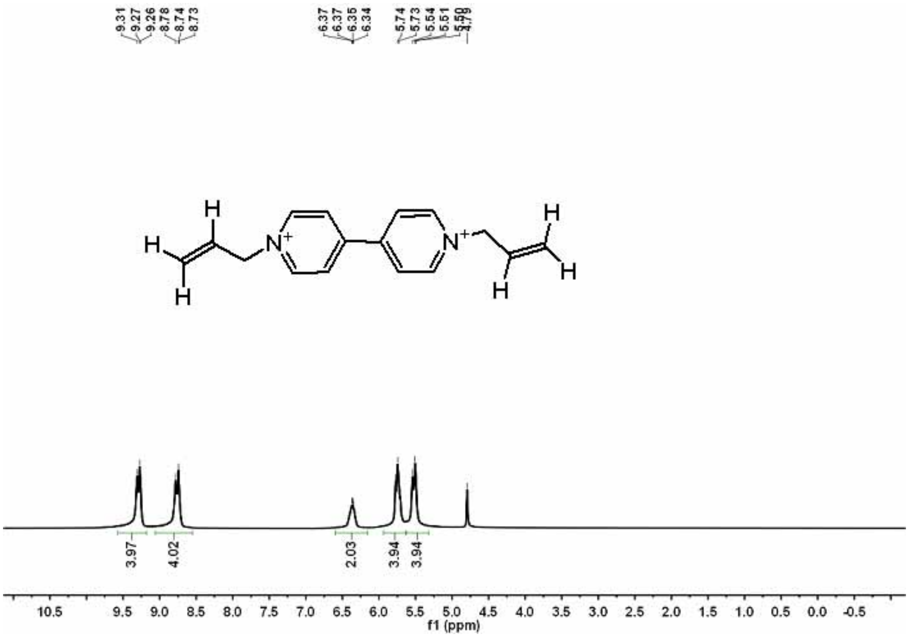


Figure S6. Contact angles which C4AE SAMs interacting with paraquat in different pH (1.0 – 14.0).

As shown in FigureS6, in general, wettability of C4AE SAMs which exposes into paraquat in phosphate buffer solution with different pH has a little change. In details, contact angle of the surface in acidic solution is relative larger than that in alkaline solution, however, the change of contact angle is less than 7º.



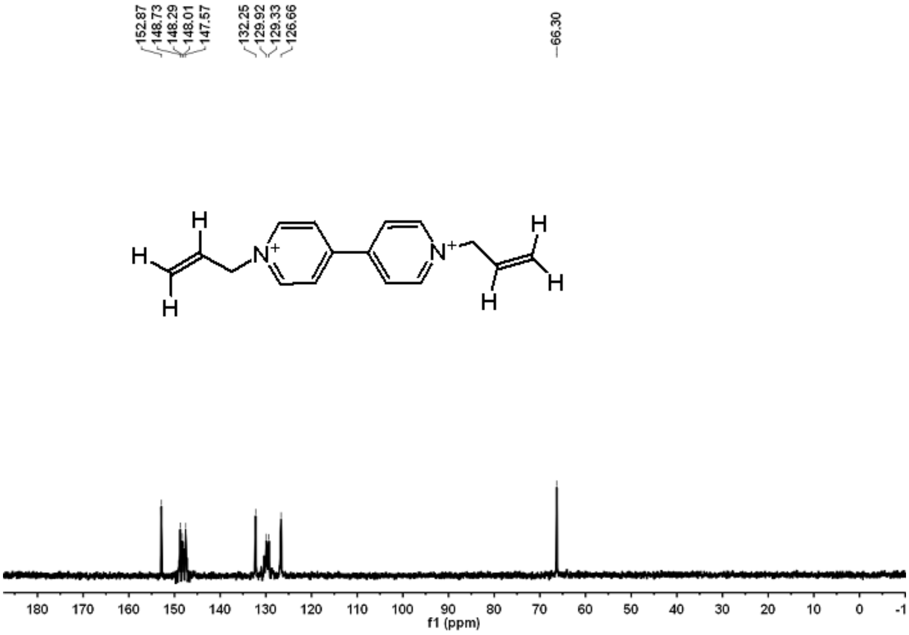


Figure S7. ^{1}H NMR and ^{13}C NMR of **c** compound.