

**Design of switchable wettability sensor for paraquat based on clicking calix[4]arene†**

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A calix[4]arene acetylene (C4AE)-modified gold surface is successfully constructed *in situ* via click chemistry. The functionalized surface is used for selective recognition of paraquat by a wettability switch. Impedance measurements showed that the surface also expresses recognition for paraquat with a high sensitivity of 10 pM. The recognition mode, based on host–guest inclusion, is studied by computational calculations and the possible mechanism is analyzed.

Self-assembled monolayers (SAMs) have been applied to recognition,<sup>1</sup> responsive materials,<sup>2</sup> electrocatalytic reduction,<sup>3</sup> and molecular electronics<sup>4</sup> because of their unique optical/electronic properties and excellent stability. Among these applications, researchers have mainly focused on molecular recognition, but our goal is setting signal switches to monitor molecular sensors. A range of control switches have been developed using functional surface layers responding to light,<sup>5</sup> temperature,<sup>6</sup> pH,<sup>7</sup> electrical signals,<sup>8</sup> *etc.* In particular, systems using guest recognition on SAMs characterized by kinds of signal change have attracted attention because of their smart physical and chemical properties, which could be developed for use in chips or micro-electrodes.

Wettability is an important optical output signal based on the contact angle. Although this is not currently given much attention, it is a suitable process for molecular recognition on SAMs because it is an important surface property and is governed by both chemical composition and geometric structure. Sun and co-workers<sup>9</sup> have performed much research in this area and have realized a wettability switch between super-hydrophobicity and super-hydrophilicity of polymers at interfaces. They reported a wetting switch for nucleotide responses to a smart polymer at micro–nano interfaces,<sup>10</sup> and developed chiral biomolecule sensors *via* a smart chirality-triggered surface polymer.<sup>11</sup> Recently, our group has found that wettability can be used for recognition of methomyl by a surface modified with a calix[4]arene lipoic acid.<sup>12</sup>

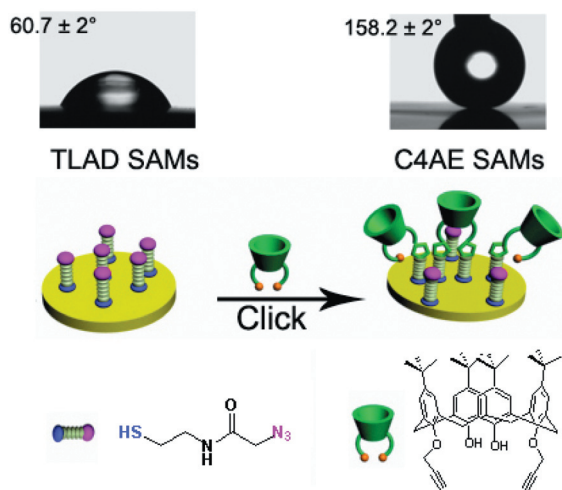
Changes in surface wettability are mainly influenced by hydrogen bonds and molecular polarity.<sup>13</sup> Functional interfaces are designed based on the principle that guest molecules could form hydrogen bonds with water or affect the polarity at the interface after they have been selected by, and interacted with, specific host molecules. Thus, calixarenes, which have efficient inclusion ability and whose upper and lower surfaces and cavities can have specific hydrophobic properties, could be considered as hosts in molecular recognition. In particular, calix[4]arene has a strong ability for recognition of guest molecules on SAMs by wettability switching. As a result, it is interesting, feasible, and of potential practical application to develop wettability switches for molecular recognition on SAMs modified by calix[4]arene.

Calix[4]arene acetylene (C4AE) clicked to a gold surface *in situ* was constructed and successfully formed C4AE SAMs. C4AE SAMs show smart super-hydrophobic properties. The hydrophobicity of C4AE can be changed by adding different guests; using paraquat as a guest causes a large change from super-hydrophobicity to super-hydrophilicity, that is, the SAMs achieve excellent selectivity for paraquat over other guests using a wetting switch. Impedance spectroscopy also indicates good paraquat selectivity, with a low limit of 10 pM. A model of the possible inclusion complex formed by C4AE with paraquat has been studied by molecular simulation and the mechanism of selective recognition has been discussed.

C4AE SAMs have been successfully produced, and the assembly process is shown in Scheme 1. 3-Azido-*N*-(2-mercaptoethyl)propanamide (TLAD) is first assembled on the gold surface through S–Au bonds, TLAD SAMs are formed; then C4AE is clicked to the TLAD SAMs *via* connection of triazoles to form C4AE SAMs. The assembly process has been tracked step-by-step by X-ray photoelectron spectroscopy (XPS), contact angle (CA), and impedance spectroscopy. The XPS of TLAD SAMs and C4AE SAMs, shown in Fig. S1 (ESI†), both contain C, O, S, and N, indicating that TLAD SAMs were successfully assembled. The element contents of C4AE SAMs and TLAD SAMs have also been analyzed by XPS and the results are shown in Table S1 (ESI†). The C content of C4AE SAMs is 69.72% and that of TLAD SAMs is 34.47%; this shows that the C content is greatly increased after C4AE clicking to TLAD SAMs. The N and S contents in the C4AE SAMs after clicking are 6.36% and 6.72%, respectively; these values are lower than

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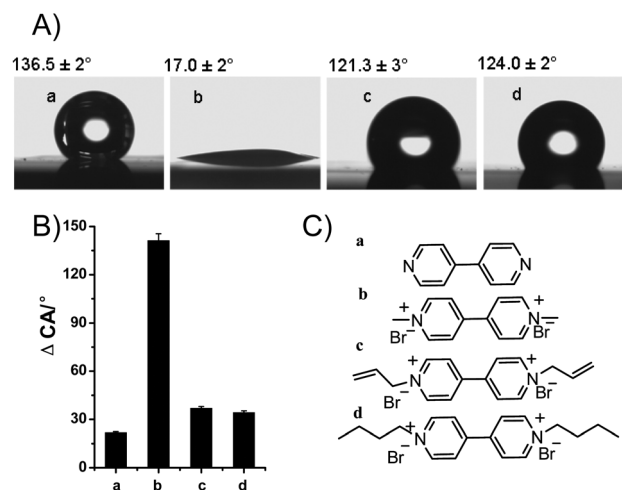
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c2ob00018k



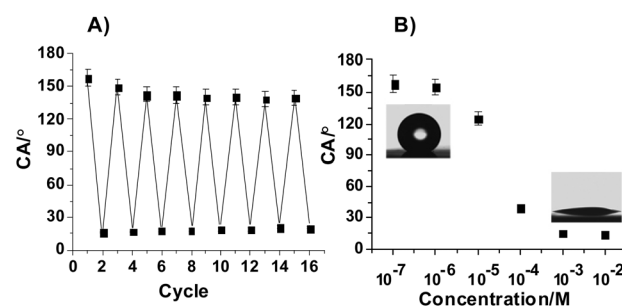
**Scheme 1** The process of C4AE SAMs formation on gold surface by clicking reaction *in situ* and contact angles on micro–nano gold surface (shown above the process); the angles indicate that super-hydrophobic SAMs are obtained.

those in TLAD SAMs (N 32.69% and S 20.26%). The experimental results for element contents are consistent with the changes calculated by theoretical analysis before and after C4AE clicking. Interestingly, the contact angles (CAs) of the C4AE SAMs and TLAD SAMs have obvious differences, as shown in Scheme 1 and Fig. S2 (ESI†). The CA of the TLAD SAMs is  $60.72 \pm 2^\circ$ , which is less than that for a bare hydrophobic micro–nano gold surface,  $124.0 \pm 2^\circ$ . The values for C4AE SAMs are  $158.2 \pm 2^\circ$  after C4AE clicking to the TLAD SAM surface, so clicking realizes super-hydrophobic supramolecular-functionalized surfaces. Moreover, the impedance values ( $R_{ct}$ ) of the bare gold surface, TLAD SAMs, and C4AE SAMs, determined by impedance spectroscopy, are 0.22, 1.18 and 2.86 k $\Omega$ , respectively, as shown in Fig. S3 (ESI†). In summary, the XPS, CA, and impedance changes in TLAD SAMs and C4AE SAMs confirm that C4AE SAMs are successfully constructed and give excellent super-hydrophobic properties on the micro–nano gold surface.

Specific C4AE SAMs could be used as molecular chemosensors. Considering the unique host C4AE, four guests, *i.e.*, compounds **a**, **b**, **c**, and **d** were selected; these compounds are a series of highly toxic pesticides. The guests are symmetric and positively charged; their structures are shown in Fig. 1C. First, the C4AE SAMs were treated with 0.05 mL of a  $1.0 \times 10^{-3}$  M solution of the four guests for 1–2 min, and then the free excess solution remaining on the surface was removed with a little water ( $0.15 \pm 0.05$  mL). The processed C4AE SAMs were dried using a  $N_2$  flow. The contact angle was measured to evaluate the effects of the four guests on the wettability. As shown in Fig. 1A, the CA decreased to  $17.0 \pm 2^\circ$  when paraquat was added; this indicates excellent hydrophilicity. The CAs of the functional SAMs treated with the other guests were more than  $120^\circ$ , indicating obvious hydrophobicity. Thus, the wettability switch from super-hydrophobicity to hydrophilicity after C4AE SAMs exposure to paraquat solution shows that C4AE SAMs have a strong ability to distinguish paraquat from the other guests.



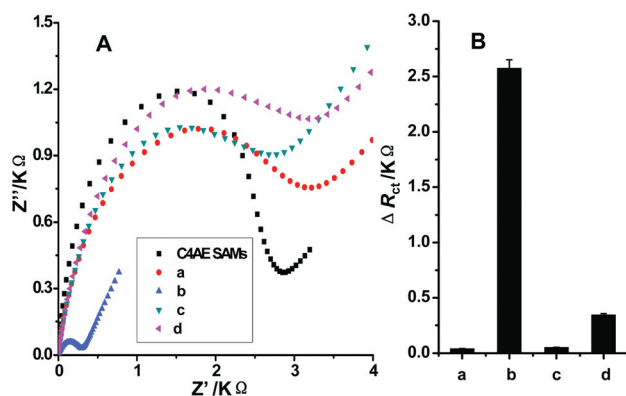
**Fig. 1** (A) CA relationship images for C4AE modified on micro–nano gold surface with the four paraquat analogs. (B) Histogram showing contact angle variations ( $\Delta CA = CA_{\text{control}} - CA$ ); these indicate that C4AE SAMs show high selectivity for paraquat. (C) The structures of the four paraquat analogs.



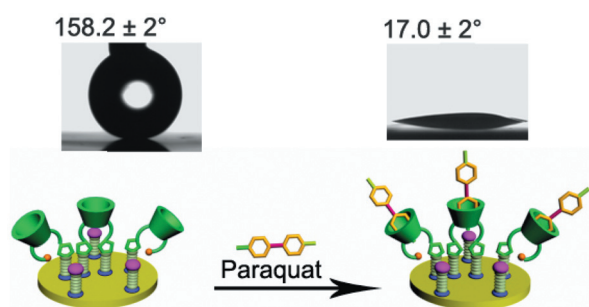
**Fig. 2** (A) Cycling experiments for the wettability switching between super-hydrophobicity and super-hydrophilicity upon alternate treatments with paraquat (0.1 mL,  $1.0 \times 10^{-3}$  M) and pure water; (B) CAs with various concentrations of paraquat (0.1 mL,  $1.0 \times 10^{-7}$  –  $1.0 \times 10^{-2}$  M).

The wettability switch successfully achieves a molecular functional surface, which could be used in molecular sensors; the method is favorable because surface recognition is clearly observed. In further studies of paraquat recognition using wettability, the effects of paraquat concentration and the reusability of the C4AE SAMs were investigated. A cycling experiment in which CAs were measured examined the reusability of the SAMs for paraquat recognition; the results are shown in Fig. 2A. The results demonstrate that the SAMs can be used at least six times, indicating that paraquat recognition on the functional surface has good reversibility. It was found that the CA changes linearly as the paraquat concentration increases from  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-2}$  M, as shown in Fig. 2B. This means that the hydrophilicity was reduced until the concentration was above  $1.0 \times 10^{-4}$  M, indicating that low concentrations of paraquat do not visibly affect wettability of C4AE SAMs.

Impedance, which is another important interface property, can also be used to monitor the guest-recognition ability of C4AE SAMs. Electrochemical impedance spectroscopy was carried out



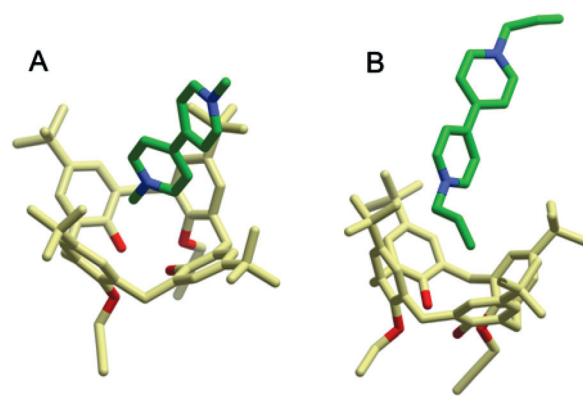
**Fig. 3** (A) Impedance response of Fe(CV)<sub>6</sub><sup>3-/4-</sup> at C4AE SAMs electrode in the presence of the four guests (1.0 × 10<sup>-4</sup> M), including compounds **a**, **b**, **c**, and **d**. (B) The histogram shows the impedance values in graph A.



**Fig. 4** Possible mechanism of C4AE interaction with paraquat on gold surface causing wettability switch between super-hydrophobicity and excellent hydrophilicity.

in mixed solutions of a redox ferricyanide probe (5.0 mM, Fe(CN)<sub>6</sub><sup>3-/4-</sup>) and each of the four guests (1.0 × 10<sup>-4</sup> M). As shown in Fig. 3,  $R_{ct}$  for paraquat on C4AE SAMs is 0.36 kΩ, which is much less than the value of 2.86 kΩ for C4AE SAMs alone; however, the values with the other three guests are more than 2.76 kΩ. These results indicate that C4AE SAMs selectively recognize paraquat from among the four analogs. In the quantitative analysis for paraquat, impedance experiments were carried out in the presence of different concentrations, ranging from 1.0 × 10<sup>-12</sup> M to 1.0 × 10<sup>-4</sup> M (Fig. S4, ESI<sup>†</sup>). A linear equation is obtained:  $R_{ct} = -0.23[C] + 2.16$ , with a linearity coefficient of 0.991. The limit of detection (3σ) for paraquat is 10 pM, indicating high sensitivity.

In summary, the results of CA changes and the large reduction in  $R_{ct}$  after exposure of C4AE SAMs to paraquat demonstrate that paraquat interacts with the smart functional C4AE on the gold surface. As shown in Fig. 4, C4AE is of low polarity, has a unique hydrophobic cavity, and four external *tert*-butyl groups at the upper rim; this results in excellent hydrophobicity (158.2 ± 2°). Paraquat has high polarity and positive charges, and is an organic ionic compound with a strong affinity for water molecules. When it enters into the C4AE cavity and is exposed to the outer surface of the SAMs, it could induce a wettability switch change from super-hydrophobicity to super-hydrophilicity. Selective recognition of paraquat was determined by the



**Fig. 5** The complex modes formed by C4AE with **b** compound (A) and C4AE with **c** compound (B), which were calculated at b3lyp/6-31G (d) levels using Gaussian 03[1] package.

effects of charge and three-dimensional space. As is well known, **b**, **c**, and **d**, but not **a**, have positive charges and the butyl group in **d** is larger than the methyl group in **b** and the allyl group in **c**. C4AE is electron-rich and its cavity is of a specific size, so **a** and **d** could not interact well with C4AE. To understand the structural features of the complexes formed between C4AE and **b** or **c**, computational calculations were carried out at the b3lyp/6-31G(d) level using the Gaussian 03[1] package.<sup>14</sup> The binding modes of the complexes formed by the host with the guests are shown in Fig. 5, and the relevant binding free energies were obtained. The calculated results show that the binding energy between C4AE and **b** is -36.97 kJ mol<sup>-1</sup>, which is lower than that for the complex between C4AE and **c** (-27.80 kJ mol<sup>-1</sup>), indicating that the complex formed between C4AE and **b** is more stable than that formed with **c**. This means that C4AE combines more readily with **b** than with the other three guests. Ferricyanide is negatively charged and is therefore close to paraquat on the surface, which leads to a large reduction of the impedance value of the functional SAMs.

In conclusion, C4AE SAMs have been successfully constructed and shown to have good selectivity for paraquat by means of a wettability switch from super-hydrophobicity to super-hydrophilicity. Impedance measurements indicated a high sensitivity of 10 pM. The high selectivity and sensitivity for paraquat by C4AE SAMs are attributed to inclusion complexes of C4AE with paraquat by host-guest interactions. This method of paraquat recognition has practical applications.

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