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Switchable Wettability Sensor for Ion Pairs Based on Calix[4]azacrown Clicking

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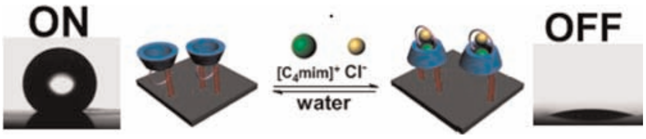
ABSTRACT



A new calix[4]azacrown is synthesized from 1,3-dipropynyloxycalix[4]arene in a good yield of 85% and was modified on a silicon surface via click chemistry to be a switchable wettability sensor for ion pairs ([C_4mim]Cl). A cooperative mechanism involving supramolecular interactions is proposed.

The design and application of ion-pair receptors, capable of the simultaneous coordination of both anionic and cationic guest species, has attracted significant interest because of their potential application as novel extraction reagents for the purification of pernicious substances in the environment.[1−3] Recently, this exciting area of ion-pair recognition has been concerned with the syntheses of host molecules that comprise binding sites for both anionic and cationic guests.[4] Calixcrowns make up a family of calixarenes that exhibit a superior recognition of ion pairs via the cooperation of both the calixarene and crown moieties.[5,6] Beer and co-workers synthesized calixcrowns with binding sites for both anionic and cationic guest species as ion-pair receptors.[3a,c,5a]

Developing a more direct, convenient, and universal technique based on the majority of host molecules is of great significance.[7] Controlling surface wettability has also attracted interest in recent years,[8] as it is important for a range of biological and chemical applications.[9] Thus, chemical, thermal, and pH-sensitive wettability sensors have been reported.[10] More recently, our group has designed a calix[4]arene modified Au surface, which exhibited a wettable and electrochemical impedance dual-signal response for methomyl.[11] In general, these sensors are controllable surfaces in terms of wettability, owing to their inherent physicochemical properties under environmental conditions. To our knowledge, wettability sensors for recognizing ion pairs have been scarcely reported.

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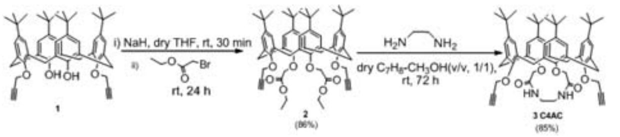
In this work, we have designed an ion-pair wettability responsive chemosensor utilizing dual-site calixazacrown-based interfacial materials. Micro/nano structured silicon surfaces, which mimic the surfaces of lotus leaves, have been selected as a substrate because they can amplify signal output with respect to wettability alteration.[12] A simple click chemistry strategy was employed to fabricate the calix[4]azacrown (C4AC) functionalized silicon substrate, which was assessed in terms of ion-pair recognition performance. The wettability of the C4AC-based surface can be modulated reversibly in the presence/absence of 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) between superhydrophobic and super-hydrophilic states. Calixazacrown-based wettability sensors are of great significance, as they find potential application as chips or materials which could monitor environmental pollution.[10a,15]

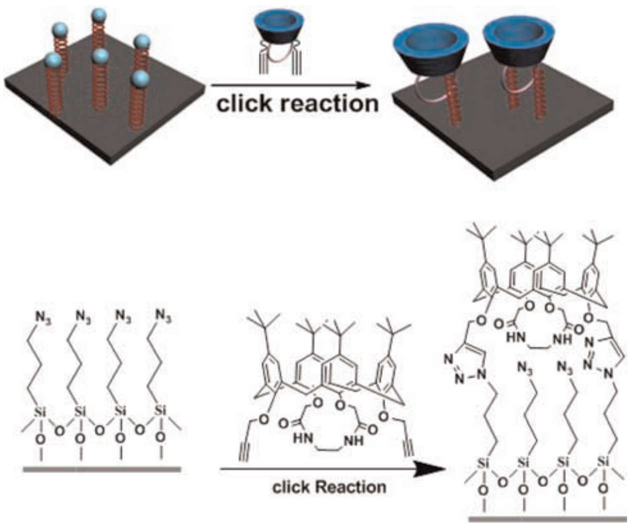
Scheme 1. Synthesis of the C4AC



The synthetic strategy toward C4AC **3** is depicted in Scheme 1. Compound **1**[16] and NaH were stirred in dry THF for 30 min, and then ethyl bromoacetate was added. The mixture was stirred at room temperature for 24 h, and the crude product was purified by recrystallization to afford **2** in 86% yield. Compound **2** and ethane-1,2-diamine were stirred in dry toluene$-$CH$_3$OH at room temperature for 72 h. The evaporated crude product was then purified by column chromatography to give a white powder **3** in 85% yield. C4AC **3** and **2** were fully characterized by NMR and ESI-MS (see the Supporting Information).

The C4AC self-assembled monolayers (SAMs) were constructed via click reactions between the Si-N$_3$ SAMs and the C4AC in CH$_3$CN (Scheme 2). The C4AC-modified silicon surfaces were characterized by X-ray photoelectron spectroscopy (XPS) and water contact angle (CA) measurement (Figures S2 and S3, Supporting Information).

Scheme 2. Clicking C4AC onto the Silicon Surface



An XPS-derived atomic concentration analysis for the SAMs revealed that the concentration of C undergoes a significant increase after the click reaction. This confirms that the click reaction has occurred. The properties of the C4AC-functionalized surfaces were studied by CA. As shown in Figure S1a (Supporting Information), the bare rough silicon wafer is superhydrophilic (3.5 ± 3°) and the CA for the Si$-$N$_3$-immobilized surface is 77.1 ± 3° (Figure S2b, Supporting Information). Postclick reaction, the C4AC-SAMs surface becomes superhydrophobic (154.6 ± 3°) due to the hydrophobic properties of the tertiary butyl within C4AC. The result indicates that the C4AC has successfully immobilized onto the silicon surface.

Considering the structure of C4AC, different organic ion pairs were selected as guests. Upon immersing the modified silicon surface in a [C$_4$mim]Cl solution, the CA was only 10.1 ± 3° (Figure 1a). However, for [C$_4$mim]PF$_6$, [C$_4$mim]Br, or a chloride source such as NaCl, the wettability of the surface remained nearly unchanged. These results indicate that the C4AC-functionalized surface exhibits a wettability response to[C$_4$mim]Cl, selectively (Figure 1 and Figure S4, Supporting Information).

Upon further treatment of the [C$_4$mim]Cl-induced hydrophilic surface (10.1 ± 3°) with water for ~5 min, the CAs reverted to their original values (~154°). This indicates a good reversibility for the [C$_4$mim]Cl-responsive wettability. In summary, this C4AC-immobilized surface can switch between high hydrophilicity and super-hydrophobicity under [C$_4$mim]Cl stimuli control. A cycling experiment (Figure 2b) also reflected a good reversibility

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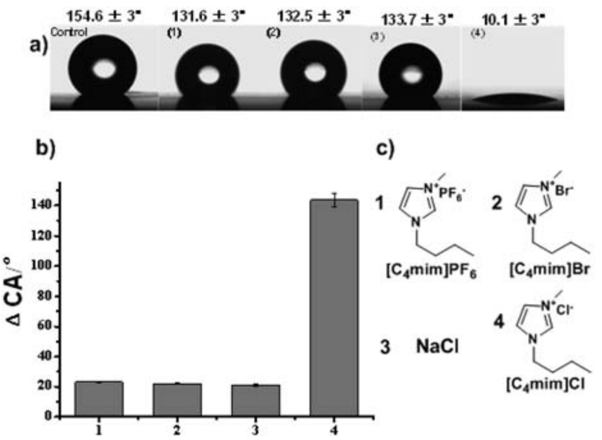

Figure 1. (a) CA relationship images for the C4AC SAMs with different guests. (b) Contact angle variation ($\Delta CA = CA_{control} - CA$) histogram for the C4AC SAMs in the presence of four guests, which indicates the selectively wettability responsive of C4AC toward [C_4mim]Cl. (c) Ion pairs.

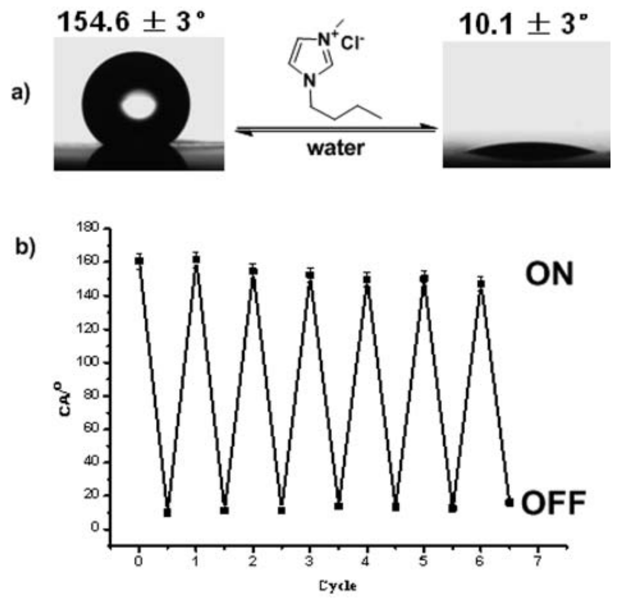

Figure 2. Cycling experiment into the wettability switching behavior of the C4AC-modified silicon surfaces upon alternate treatment with [C_4mim]Cl and water, which indicates a good reversibility between superhydrophobicity and high hydrophilicity.

for this property, which could find wide applications in a diverse range of fields.

To study the mechanism of this binding, some control experiments were performed. First, the inorganic chloridum had no effect on the wettability of the C4AC-SAMs surface (Figure S4, Supporting Information). This indicates that the imidazolium ion is a suitable cation for recognition. Second, host compound **1** (1,3-dipropynyloxycalix[4]arene) was grafted onto a silicon surface to study its identification. The chloridum did not change the water contact angle of the compound **1** SAMs, which suggests the C4AC azacrown unit is important for chloride recognition within [C4mim]Cl (Figure S5, Supporting Information). UV–vis absorption spectra were employed to study both the binding model and stoichiometry between the C4AC and [C4mim]Cl. As illustrated in Figure S6 (Supporting Information), upon the addition of [C4mim]Cl to C4AC in $CHCl_3$, the absorption maxima at 268.1 nm is reduced. This indicates the formation of a C4AC–[C4mim]Cl complex. Meanwhile, a Job plot, as shown in Figure S8 (Supporting Information), has a peak at 268.1 nm with a molar fraction of 0.5. This suggests a binding stoichiometry of 1:1.

To obtain further insight into the mechanism, NMR experiments were carried out. As shown in Figure S13 (Supporting Information), upon treatment with 1 equiv of C4AC, the signals for the NCH=CH group underwent an upfield shift (H_2 = 0.088 ppm; H_3 = 0.055 ppm), and protons for NCH_3 exhibited an upfield shift (H_1 = 0.010 ppm). The chemical shift change is small, possibly owing to weak hydrophobic interactions.[17] Furthermore, a 2D NOESY spectrum revealed intermolecular nuclear Overhauser effects (NOEs) between the tertiary butyl (H_A, C(CH_3)) and the methane of the azacrown unit (H_B, NH(CH_2)$_2$NH) (Figure S14, Supporting Information). These results indicate that the [C_4mim]Cl interacts with the C4AC cavities and cone to 1,3-alternate conversion of C4AC in the presence of [C_4mim]Cl. Moreover, calix[4]azacrown without the coupling group was employed to study the binding mode, as shown in Figure S15, Supporting Information. It shows a similar binding behavior to further prove the complexation mechanism.

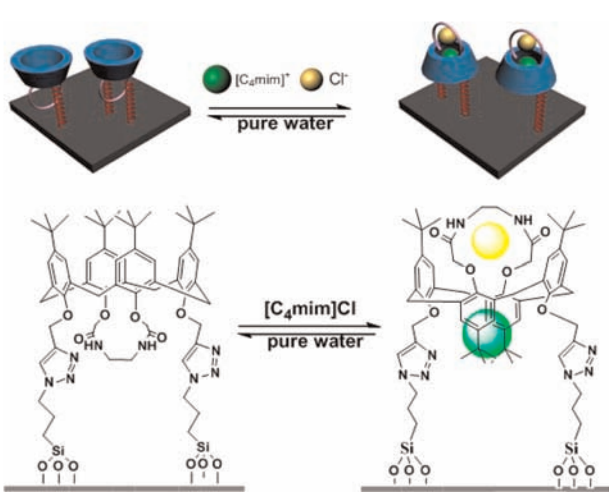

Figure 3. Proposed interactions between the C4AC-SAMs and the [C_4mim]Cl ion pairs on the silicon surface. The chloride ion is yellow and the imidazolium salt ion is green.

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On the basis of these results, a cooperative molecular mechanism is proposed for the ion-pair responsive wettability (Figure 3). Initially, the tertiary butyl groups of the C4AC result in a relatively hydrophobic behavior for the silicon surface. Upon exposure to [C_4mim]Cl, the 1-butyl-3-methylimidazolium ([C_4mim]) can interact with the cavity of the calix[4]arene through both $\pi-\pi$ and cation$-\pi$ interactions.[14] Meanwhile, the [C_4mim] can induce a reversion in terms of calix[4]azacrown conformation. The azacrown unit can then combine with chloride via hydrogen-bonding interactions. The introduction of [C_4mim]Cl leads to a hydrophilic behavior for the silicon surfaces. The cooperative effects result in an excellent [C_4mim]Cl responsive wettability, which allows a reversible switching between superhydrophobicity and high hydrophilicity.

In conclusion, a smart calix[4]arene surface has been prepared via click chemistry. The surface exhibits an excellent reversible wettability response to [C_4mim]Cl, which could be applied for ion-pair recognition in fields including biomimetics and biochips. The most promising potential application could be for environmental monitoring and purification of pernicious substances in the environment.

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Supporting Information Available. Experimental details, NMR spectra, and XPS and UV spectra. This material is available free of charge via the Internet at http://pubs.acs.org

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The authors declare no competing financial interest.