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Molecular Switches

A Photoresponsive Wettability Switch Based on a Dimethylamino Calix[4]arene

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Abstract: A photoreversible switch based on a photoresponsive host–guest system consisting of dimethylamino calix[4]arene **L** and 4-(phenylazo)benzoic acid (**O**) is reported. The host **L** exhibited selective binding and release of **O** on UV and visible irradiation at 450 and 365 nm, respectively. Moreover, the photoresponsive host–guest complex was applied as a photocontrolled wettability switch on a functional micro/nanostructured silicon surface, and is thus promising for applications in sensors and microfluidic devices.

Introduction

Photoresponsive switches have attracted much interest due to their various applications such as smart materials, drug-delivery systems, sensors, protein probes, and functional nanodevices.[1–4] For instance, Ogoshi et al. described photoreversible switching in a photoresponsive host–guest system of pillar[6]-arene with triethylene oxide substituents and an azobenzene derivative in aqueous solution.[5] However, most of the reported photoresponsive switches operate in the solution phase. The development of photoresponsive switches on functional surfaces has attracted a lot of attention because of potential applications in chip fabrication and materials science.

Photoresponsive switches on a functional surface undergo reversible changes in their properties when illuminated by light of an appropriate wavelength.[6] Wettability of the surface is an important property of a solid material, which can be reversibly changed between hydrophobic and hydrophilic states.[7] It is affected both by the structure and chemical composition of the material. For example, micro/nanostructured silicon surfaces, which mimic the surfaces of lotus leaves, were selected as substrates because they can amplify signal output with respect to alterations in wettability. The fabrication of photoresponsive systems on solid surfaces is of vital importance in functional applications.[8] Therefore, it is necessary to develop a photoreversible host–guest system on the functional surface. Calixarenes, which are third-generation supramolecules with cuplike shape and easy functionalization, have outstanding ability to selectively bind different kinds of guests and provide a useful platform for the construction of various interesting supramolecular systems.[9] For example, *trans*-azobenzene can form an exact 1:1 inclusion complex with calixarene by being strongly bound in the cavity of the calixarene, whereas the *cis* form can rapidly slide out of the cavity, and the *cis*–*trans* isomerization can be reversibly switched on external photoirradiation at 450 and 365 nm in the solution phase.[10] Moreover, this system is still effective on solid substrates, and has been studied for many applications, including photoresponsive sensors, microfluidic devices, and more sophisticated photoresponsive supramolecular systems. Furthermore, it may be used in diverse medical and biological fields.[11]

The purpose of our research was to synthesize a new calixarene for the development of a novel micro/nanostructured interface that can recognize *trans*-4-(phenylazo)benzoic acid (*trans*-**O**) and thus obtain a photoresponsive switch. Because dimethylamino groups have basic properties, the central N atom exhibits stronger electronegativity and higher molecule-adsorbing speed.[12] Thus, it can more easily interact with azo acids. We synthesized a novel deep-cavity calix[4]arene with dimethylamino groups on the upper rim. It has a better inclusion performance because of the interaction between dimethylamino groups and azo acids.[13] Further, dimethylamino groups are strongly hydrophobic. We fabricated a reversible photoresponsive host–guest system from dimethylamino calix[4]arene **L** and **O**, which was characterized by fluorescence (FL), UV, and ^{1}H NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and TEM. Host **L** exhibited selective binding and release of **O** under UV and visible irradiation at 450 and 365 nm, respectively. Furthermore, the host–guest system was introduced onto a functional micro- and nanostructured silicon surface to form a photocontrolled wettability switch. We anticipate that this research can offer a feasible method for introducing photoinduced wettability properties on solid surfaces.

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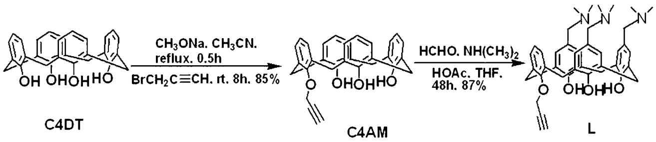
Results and Discussion

Synthesis and characterization of receptor L and its complexation with *trans*-O

The synthetic strategy for **L** is depicted in Scheme 1. Calix[4]arene (C4DT, 2.4 mmol) and sodium methylate (2.8 mmol) were stirred in refluxing acetonitrile for 0.5 h, and then propargyl bromide (0.5 mL) was added.[14] The mixture was stirred at room temperature for 8 h, and the crude product was purified by column chromatography to give propinyl calix[4]arene C4AM (Supporting Information, Figure S1) in 85 % yield. Subsequently, C4AM (1.0 mmol), dimethylamine (5.0 mmol), formaldehyde (5.0 mmol), and acetic acid (5.0 mmol) were stirred in THF at room temperature for 48 h.[15] After solvent evaporation, the crude product was purified by column chromatography to give **L** as a white powder in 87 % yield, which was characterized by NMR spectroscopy and ESI-MS. As shown in Figure S2 (Supporting Information), the ^{1}H NMR spectrum of **L** exhibited a pair of doublets for the bridging methylene groups at 4.29 and 4.59 ppm, a single peak for the alkynyl group at 2.79 ppm, and two singlets for the dimethylamino groups at 2.17 and 2.29 ppm. All of these indicated a cone conformation of **L**. The ^{13}C NMR spectrum (Supporting Information, Figure S3) further corroborated the cone conformation of **L** by the presence of a peak for the methylene groups. The ESI mass spectrum (Supporting Information, Figure S4) showed a molecular-ion peak for **L** at *m/z* 634.2.



Scheme 1. Synthesis of **L**.

To investigate the interaction between **L** and **O** under UV irradiation, a fluorescence experiment was performed with an excitation wavelength of 280 nm (Figure 1). Equal equivalents of **O** and **L** were dissolved in CH_3OH solution, and the solution was irradiated successively with UV and visible light for 30 min. As shown in Figure 1, a distinct decrease in fluorescence was observed after UV irradiation at 365 nm. The fluorescence intensity after further irradiation with visible light was almost the same as that before UV irradiation and indicated FL recovery of the **L**⊃**O** complex.

To prove good photoresponsive properties of the host–guest system, UV/Vis spectroscopic studies were carried out (Supporting Information, Figure S6). The UV/Vis spectrum for equal equivalents of **O** and **L** in CH_3OH solution before irradiation with 365 nm UV light is shown in Figure S6 a of the Supporting Information. On irradiation with UV light at 365 nm, the absorption band of the above system around 332 nm decreased remarkably, and concurrently the band at around 445 nm increased slightly. The absorption bands of the azobenzene unit at 332 and 445 nm are ascribed to π–π* and n–π* transitions, respectively. The changes of the absorption bands induced by UV irradiation indicated photoisomerization of *trans*-**O** to *cis*-**O**. On the contrary, after further irradiation with visible light, the absorption band at 445 nm corresponding to *cis*-**O** decreased, while the absorption band at 332 nm corresponding to *trans*-**O** increased; this indicates isomerization of *cis*-**O** to *trans*-**O**. Furthermore, the linear plot in Figure S6 b of the Supporting Information showed that the *cis* isomer of **O** undergoes *cis*-to-*trans* back-isomerization in solution on irradiation with visible light centered at 450 nm.

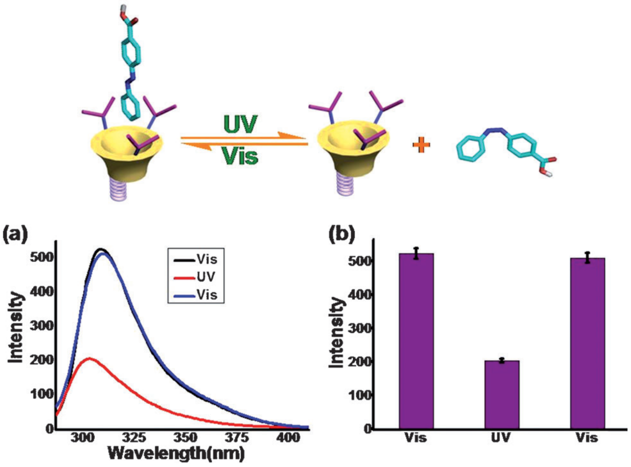


Figure 1. a) FL spectra of equal equivalents of **O** and **L** mixed in CH_3OH solution before irradiation (black line), after irradiation with 365 nm UV light (red line), and after further irradiation with visible light (blue line). b) Histogram of FL intensity variation confirming photoresponsive switching.

TEM was used to investigate the difference in the structures of the **O**/**L** system in solution before and after UV irradiation (Supporting Information, Figure S7). Figure S7 a shows spherical particles of size 60–110 nm for the solution of the **L**⊃**O** complex before irradiation with 365 nm UV light. Spherical particles of larger size (200–250 nm) were observed on irradiation with 365 nm UV light (Supporting Information, Figure S7 b). After further irradiation with visible light, the size of spherical particles was reduced drastically to 80–140 nm (Supporting Information Figure S7 c). This can be attributed to the increased assembly driving force of π–π stacking interactions on irradiation with 365 nm UV light (Supporting Information, Figure S8).[16]

To further verify the binding between **L** and *trans*-**O**, ESI-MS analysis was carried out. The molecular-ion peak observed at *m/z* 860.0 in the ESI mass spectrum (Supporting Information, Figure S5) can be attributed to the **L**⊃**O** complex. The molecular-ion peak of **L** alone was observed at 634.2. The whole ESI-MS study fully explained the above switching process and also confirmed the formation of a 1:1 complex between **L** and **O**. Furthermore, a 1:1 binding stoichiometry of the **L**⊃*trans*-**O** complex between **L** and *trans*-**O** was also obtained from a Job's plot of UV titration data, which had a peak at 322.5 nm with a molar fraction of 0.5 (Supporting Information, Figure S9).

To further confirm the above conclusions, ^{1}H NMR spectroscopy (Figure 2 and Figure S10) was conducted to provide evi-

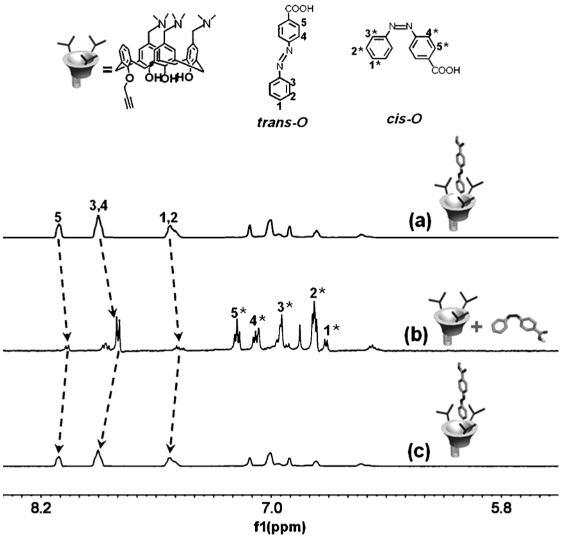


Figure 2. a) ^{1}H NMR spectra of **L** and **O** (both 6 mм, CD_3OD, 600 MHz, 298 K) before irradiation with 365 nm UV light. b) ^{1}H NMR spectra of **L** and **O** after irradiation with 365 nm UV light. c) ^{1}H NMR spectroscopy of **L** and **O** after further irradiation with visible light. Thus, photoresponsive switching was confirmed by ^{1}H NMR spectroscopy.

dence about the interaction of *trans*-**O** with **L**. Generally, the *trans* form is preferred for azobenzene derivatives in [D$_4$]MeOH. When a solution of *trans*-**O** was irradiated by UV light for 30 min, the ratio of the *trans* to the *cis* form changed to about 50:50, that is, there was an equilibrium between *trans*-**O** and *cis*-**O**. However, *cis*-**O** is not very stable, undergoes quick total transformation into stable *trans*-**O**, and the system reverts to the original state. In addition, when one equivalent of **L** was added to a solution of *trans*-**O**, chemical-shift changes were observed for protons of *trans*-**O**. Protons H^1, H^2, and H^3 showed greater shifts than H^5. This indicated that the carboxyl group was exposed outside the cavity of the calixarene and the benzene ring was inserted into the upper rim of the cavity. On irradiation with visible light at 450 nm for a sufficient time, *cis*-**O** was converted back to *trans*-**O**, and the proton signals in Figure 2c were the same as those in Figure 2a.

Application as a photoresponsive wettability switch

On the basis of the above photoresponsive switching in methanol solution, we also tried to fabricate a photoresponsive wettability switch on a silicon surface. Micro/nanostructured and functional silicon surfaces could reversibly switch *cis*-**O** and *trans*-**O** between hydrophobic and hydrophilic states under UV radiation. When the **L**⊃**O** complex was formed between **L** and *trans*-**O** on the functional surface, we defined the state as wettability "off". When **O** was released from the **L**⊃**O** complex under irradiation with 365 nm UV light on the functional surface, we defined the state as wettability "on". The properties of the **L**-loaded silicon surfaces were studied by contact-angle (CA) analysis. The bare rough silicon wafer was superhydrophilic (CA = 5.0 ± 2.0°), and the CA of the Si-N_3-functionalized surface was 75.2 ± 2.0°. After the click reaction to form a self-assembled monolayer (SAM) of **L** (**L**-SAM), the surface became hydrophobic (CA = 138.6 ± 2.0°) because of the hydrophobic properties of the dimethylamino moieties of **L** (Figure 3 and Supporting Information, Figure S11). Therefore, we concluded that a functional **L**-SAM was constructed perfectly. The **L**-modified silicon surfaces were characterized by X-ray photoelectron spectroscopy (XPS; Supporting Information, Figure S12). XPS analysis of the atomic concentrations of the SAM showed a significant increase in the concentration of carbon and an obvious decrease in the concentration of oxygen after the click reaction. This indicated that the click reaction had occurred.

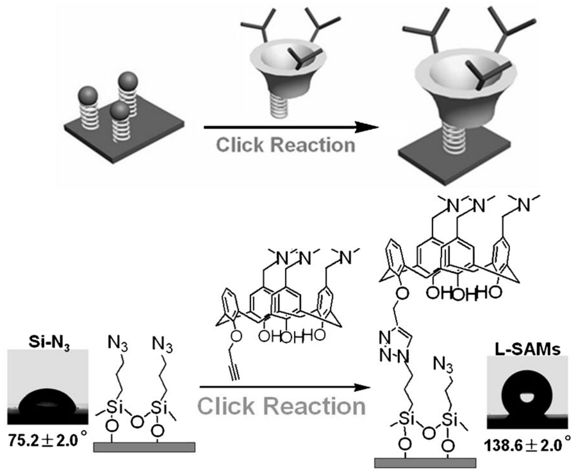


Figure 3. Formation of **L**-SAMs by click reaction.

We selected **O** as the guest for **L**-SAM on the functional silicon surface, because of the strong interaction between **L** and *trans*-**O**. The transition from hydrophilicity to hydrophobicity was proved by CA measurements. An aqueous solution of *trans*-**O** was dropped onto the **L**-modified silicon surface. After 15 min of incubation, the CA was 23.7 ± 2.0°. On irradiation with UV light at 365 nm, the CA changed to 138.6 ± 2.0°. Thus, UV irradiation altered the wettability of the surface from hydrophilic to hydrophobic. This can be attributed to the isomerization from *trans*-**O** to *cis*-**O** triggered by UV irradiation and subsequent release of **O** from the **L**⊃**O** system. Certainly, the micro/nanostructured silicon surfaces can also amplify signal output with respect to wettability alteration.[17] Moreover, in a cycling experiment six on/off cycles were achieved by alternating UV/Vis irradiation (Figure 4 and Supporting Information, Figure S13).

Conclusion

We have synthesized novel dimethylamino calix[4]arene **L**, which exhibited strong binding capacity toward *trans*-**O**, which was characterized by FL, UV, and ^{1}H NMR spectroscopy and ESI-MS. Furthermore, UV/Vis irradiation triggered photoreversible switching between binding and release of guest molecule **O** by host molecule **L** owing to *cis*–*trans* isomerism of **O**,

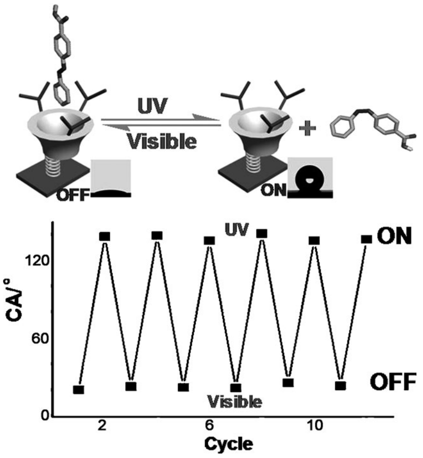


Figure 4. Cycling between CAs before and after irradiation with 365 nm UV light on the **L**-modified silicon surface, showing six switching cycles between hydrophobic and hydrophilic states.

which was verified by FL, UV, and ^1H NMR spectroscopy, ESI-MS, and TEM. This host–guest system was further coupled onto a micro/nanostructured silicon surface through click chemistry to act as a highly sensitive photoresponsive wettability switch triggered by UV/Vis irradiation. The fabricated photoresponsive host–guest system is promising in potential applications such as sensors and microfluidic devices.[18]

Experimental Section

Materials and instrumentation

^1H and ^{13}C NMR spectra were recorded on Varian Mercury VX400 instrument at ambient temperature with TMS as internal standard. ESI-MS was performed on a Finnigan LCQ-Advantage instrument. The static CA of water was measured at 25 °C by means of an OCA 20 contact angle system (Dataphysics, Germany). FL spectra were recorded on a Varain Cary Eclipse instrument. XPS was carried out on a Kratos XSAM800 photoelectron spectrometer (FRR mode).

All chemicals were of A.R. grade and were purified by standard procedures. Mill-Q water was used to prepare all solutions in this study.

Synthesis of organic compounds

Propinyl calix[4]arene C4AM: C4DT (2.4 mmol) was dissolved in acetonitrile (150 mL), sodium methylate (2.8 mmol) was added, and the mixture stirred and heated to reflux for 0.5 h. Subsequently, propargyl bromide (0.5 mL) was added, and then the mixture was stirred for 8 h. The crude product was purified by column chromatography (SiO_2, petroleum ether/chloroform 3/1) to give C4AM in 85% yield. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.67$ (s, 1H, ArOH), 9.08 (s, 2H, ArOH), 7.09–6.98 (m, 9H, ArH), 6.69 (s, 3H, ArH), 4.95 (s, 2H, $ArOCH_2$), 4.49–4.46 (d, $J = 13.2$ Hz, 2H, $ArCH_2Ar$), 4.29–4.25 (d, $J = 18.9$ Hz, 2H, $ArCH_2Ar$), 3.49–3.46 (d, $J = 13.8$ Hz, 4H, $ArCH_2Ar$), 2.75 (s, 1H, $C\equiv CH$); elemental analysis (%) calcd for $C_{31}H_{26}O_4$: C 80.50, H 5.67; found: C 80.42, H 5.52.[14]

Dimethylamino calix[4]arene L: C4AM (1.0 mmol) was dissolved in THF (40 mL) and then acetic acid (5.0 mmol) was added. Subsequently, dimethylamine (5.0 m mol) was dripped into the system. Later, formaldehyde (5.0 m mol) was added and the mixture was stirred for 8 h. Finally, **L** was produced. The product was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether 2/10) to give **L** as a white powder in 87% yield. ^1H NMR (600 MHz, CD_3OD): $\delta = 7.00$ (s, 2H, ArH), 6.93 (s, 2H, ArH), 6.88 (s, 2H, ArH), 6.81 (s, 2H, ArH), 6.59 (s, 1H, ArH), 4.64 (s, 2H, OCH_2), 4.59–4.57 (m, 4H, $ArCH_2Ar$), 4.29–4.27 (d, $J = 12.5$ Hz, 4H, $ArCH_2Ar$), 3.45 (s, 6H, NCH_2), 2.79 (s, 1H, $C\equiv CH$), 2.29 (s, 6H, NCH_3), 2.17 (s, 12H, NCH_3). ^{13}C NMR (100 MHz, DMSO) δ: 155.47, 154.57, 153.47, 134.06, 132.75, 130.10, 129.57, 128.59, 127.74, 126.41, 123.53, 122.40, 80.50, 77.60, 62.28, 61.35, 59.78, 45.41, 44.08, 43.77, 42.43, 32.36, 30.97; MS (EI+): $m/z = 633.8$ $[M]^+$ (80%); elemental analysis (%) calcd for $C_{40}H_{47}N_3O_4$: C 75.80, H 7.47, N 6.63; found: C 75.70, H 7.41, N 6.53.

Fabrication of L-modified silicon surface

Fabrication of the micro/nanostructured Si surface: A silicon wafer was used as the smooth substrate. The structured silicon substrate was fabricated by using a combination of photolithography and the inductively coupled plasma deep-etching technique to obtain a patterned silicon micropillar structure on the silicon wafer. The rough surface showed a geometrical pattern of square pillars 20 μm high, 9 μm long and with an interpillar spacing of 12 μm on a flat silicon wafer.[19]

Preparation of the Si-N_3-modified silicon substrates: The surface-structured silicon substrates, cut into 1×1 cm square pieces, were soaked in chromosulfuric acid solution for 30–60 min, rinsed with double-distilled water, and dried under a stream of N_2 gas. The cleaned wafers were immersed in an aqueous solution of NaOH (0.1 molL^{-1}) for 6 min and subsequently in aqueous HNO_3 (0.1 molL^{-1}) for 12 min to generate surface hydroxyl groups. The silicon substrates were washed with an excess of water, dried under a stream of N_2, and immersed in a refluxing 5 wt% solution of triethoxysilane azide (Si-N_3) in dry toluene (10 mL) at 110 °C for 6 h. Then the silicon wafer was washed with toluene and ethanol to remove residual Si-N_3 and dried under a stream of N_2 gas.

Click reaction between Si-N_3 and L on the silicon surface: The silicon surfaces modified with Si-N_3 were immersed in a solution of **L** in CH_3OH (10^{-2} M), to which a mixture of copper sulfate (10^{-6} M) and sodium ascorbate (10^{-7} M) was added. This solution was kept at 75 °C for 8 h. Then the silicon wafers were washed with little CH_3OH and dried under a stream of N_2 gas.

Wettability measurements on modified silicon surfaces: The wettability of **L**-modified silicon surface was evaluated by CA measurement with a 1.0 μL water droplet. Side-view photographs were recorded after a contact time of 5 min. The **L**-modified silicon wafer was incubated in a solution of the guest *trans*-**O** (0.1 mL, 1.0 mM) in CH_3OH for 10 min to form the **L**⊃**O** complex on the surface, and then washed with water and dried under a stream of N_2 gas for CA evaluation. The above modified silicon surface was immersed in CH_3OH and irradiated by UV for 30 min, and then dried under a stream of N_2 gas for CA evaluation. Then, the modified silicon surface was also irradiated by visible light for 30 min and dried under a stream of N_2 gas for CA evaluation.

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Keywords: azo compounds · calixarenes · click chemistry · molecular devices · surface chemistry

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FULL PAPER

Molecular Switches

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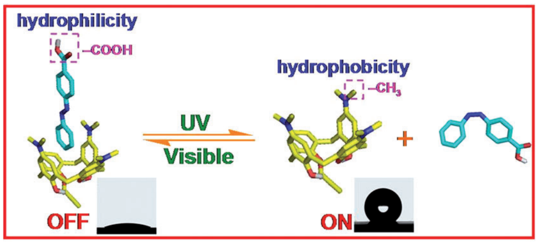
A Photoresponsive Wettability Switch Based on a Dimethylamino Calix[4]arene



Photoreversible switching of the host–guest system of dimethylamino calix[4]arene (**L**) and 4-(phenylazo)benzoic acid (**O**) is reported. Host **L** exhibited selective binding and release of **O** under UV and visible irradiation at 450 and 365 nm, respectively. Moreover, the **L**⊃**O** complex was applied as a photocontrolled wettability switch on a functional micro/nanostructured silicon surface with reversible switching between hydrophilic and hydrophobic states (see figure).