Tuning surface wettability through photocontrolled reversible molecular shuttle†

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A photocontrolled molecular shuttle SAM based on an α-cyclodextrin (α-CD)/azobenzene inclusion complex on rough gold surfaces is fabricated, which can reversibly switch the surface wettability by transferring external energy (light) to molecular mechanical motion.

The chemistry of constructing macroscopic object motion has attracted enormous interests in recent years.[1] Meanwhile, the motion of microscopic objects, *e.g.* artificial molecular shuttles, in which a ring moves back and forth like a shuttle between two stations in response to external stimuli in solution[2–4] and on surfaces,[5] meets the requirements in many potential fields of research and applications. With the development of stimuli-responsive materials,[6] reversible molecular motion, especially, the molecular mechanical movement on a surface, which is responsible for the switching of surface properties, *e.g.* surface wettability, friction, *etc.* and for the transformation of external stimuli into mechanical energy, is very promising in the field of molecular motors and energy convertors.[5] Artificial molecular shuttles formed on the basis of host–guest interaction of azobenzene and α-CD are mostly studied in solution.[3] Our group has fabricated a stimuli-responsive vesicle that can undergo reversible assembly and disassembly by using photocontrolled inclusion and exclusion reaction of an azobenzene-containing surfactant with α-CD.[4] However, few studies on self-assembled monolayers (SAMs) of molecular shuttles based on α-CD and azobenzene on gold surfaces and their behavior, such as switching the surface wettability by transferring external energy (light) to molecular mechanical motion to alter the surface free energy, have been reported.

In this communication, we demonstrate the use of self-assembled monolayers of a photocontrolled molecular shuttle on the basis of an α-CD/azobenzene inclusion complex for macroscopically tuning surface wettability, which can be reversibly changed between hydrophobicity and hydrophilicity with UV/visible irradiation. The surface wettability switches unconventionally from hydrophilic to hydrophobic under UV irradiation compared to the traditional wettability change from the photoisomerization of *trans*- to *cis*-azobenzene monolayers[7] under UV irradiation.

To produce such a surface, we have used a method that combines rough surface amplification and the SAM generated by assembling a pre-formed inclusion complex. The complex of α-CD-wrapped fluorinated azobenzene can undergo photocontrolled inclusion and exclusion reaction reversibly (Fig. 1).[3,4] The rough surface used in our experiments is formed by electrodeposition on a gold covered surface, which is well described and characterized in our previous published work, and can amplify the photo-responsive change of the wetting properties.[6a]

To realize the photocontrolled assembly and disassembly on surfaces, we synthesized the azobenzene derivatives 10-[4-(4-trifluoromethylphenylazo)phenoxy]decane-1-thiol (denoted CF_3AzoSH, shown in Fig. 1) and 10-(4-phenylazophenoxy)-decane-1-thiol (termed AzoSH) (see ESI†). The fluorinated azobenzene and α-CD can form an inclusion complex which behaves as a hydrophilic group because of the hydrophilicity of the outer part of α-CD.[3,4] When *trans*-azobenzene is transformed to *cis*-azobenzene upon UV irradiation at 365 nm, the bulky *cis* form cannot be included into the α-CD cavity anymore because of the mismatch between the host and the guest in shape, acting as a hydrophobic group because of the hydrophobic fluorinated azobenzene part.[7] Meanwhile, the fluorocarbons of the fluorinated azobenzene may act as a blocking group for α-CD by means of electronic interactions.[8] Besides the fluorinated azobenzene as the responsive moiety, the introduction of a thiol group allows for the chemisorption of CF_3AzoSH on gold coated surfaces, leading to the formation of SAMs.[9] Therefore, the inclusion complex, α-CD/CF_3AzoSH, is a suitable candidate for tuning the surface wetting properties.

We have applied the following procedure to form the SAM of α-CD/CF_3AzoSH inclusion complexes on gold surface. First, the gold covered substrate was immersed into an ethanol solution of n-C_4H_9SH for 6 min of chemisorption, taking up some sites of the gold surface.[9d] Then, immersion of the above treated substrate into a solution of α-CD/CF_3AzoSH inclusion

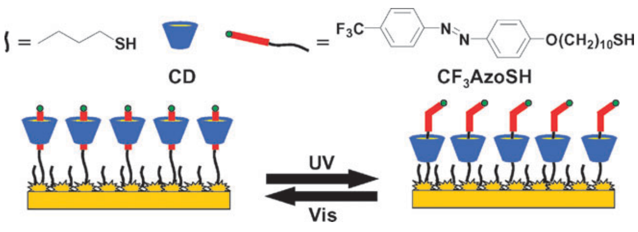

Fig. 1 Photocontrolled reversible molecular shuttles on a rough surface.

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complex led to formation of a mixed SAM of α-CD/CF_3-AzoSH and n-C_4H_9SH (Fig. S1, ESI†). The loosely packed SAM provides more free space for the photoisomerization of CF_3AzoSH between the *cis* and the *trans* form and the photocontrolled up-down motion of α-CD in CF_3AzoSH-SAMs on gold substrates upon UV/Vis irradiation. The XPS peaks of S 2p (162.05 eV, from both n-C_4H_9SH and CF_3-AzoSH) and F 1s (688.10 eV, CF_3AzoSH) clearly indicate that the α-CD/CF_3AzoSH inclusion complexes are chemisorbed onto the gold substrates. From the binding energy and the elemental composition of the SAMs, the ratio of n-C_4H_9SH and α-CD/CF_3AzoSH is estimated to be 5 : 1 (Table S1†).

We wondered if these α-CD/CF_3AzoSH-SAMs can behave as photo-responsive surfaces. In order to address this issue, contact angle (CA) measurements were employed to observe the differences in wetting properties under UV/visible irradiation. CA measurements were first performed on the n-C_4H_9SH-α-CD/CF_3AzoSH-SAMs on a rough gold surface obtained with an electrodeposition time of 3200 s at −200 mV. Before UV irradiation, the CA of the n-C_4H_9SH-α-CD/CF_3-AzoSH-SAM is 70 ± 2°. After exposure to UV light (365 nm) for 20 min, its CA becomes 120 ± 2°. There is a significant change of 50° for its CA before and after UV irradiation. The reason for this remarkable change should be the photo-controlled up-to-down molecular motion of α-CD in CF_3AzoSH-SAMs on gold surfaces. Furthermore, the CA was restored to its initial state when the surface was irradiated with visible light (450 nm) for 1.5 h, as shown in Fig. 2(a), which responds to the photocontrolled down-to-up molecular motion of α-CD in CF_3AzoSH-SAMs on gold surfaces. From Fig. 2(a), the CAs of n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified rough surface are 67.5, 71.0 and 72.1° after several cycles of the photoisomerization. The changes of the CA are small, indicating slight changes of the n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified rough surface each time. Fig. 2(b) shows photographs of the water drop profile before and after UV irradiation, and this change of wetting properties is reversible for many cycles. However, in the control experiment, the CA change of the non-fluorinated n-C_4H_9SH-α-CD/AzoSH-SAMs on a rough gold surface is not reversible (Fig. S4†). One possible reason is that the α-CD of α-CD/AzoSH-SAM has been shuttled out of the AzoSH-SAMs after several cycles. So in the process of the up-down motion of α-CD in CF_3AzoSH-SAMs on gold substrates, the fluorocarbons of the fluorinated azobenzene may act as the blocking group for α-CD by means of electronic interactions.[8] It should be pointed out that, on a flat smooth surface, the CA change is not that large, only about 2° difference (Fig. 2(a)) before and after UV light irradiation. These results clearly show that the response can be greatly enhanced by using a rough surface.[6a]

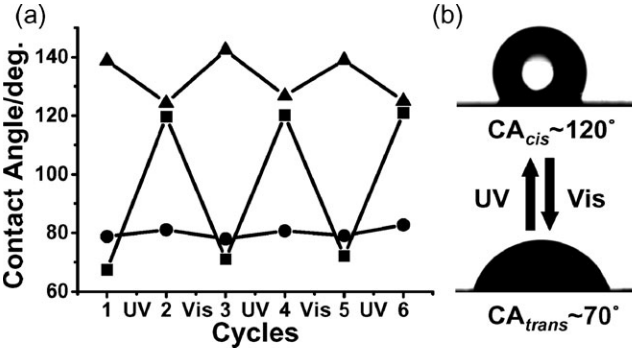

Fig. 2 (a) Reversible wettability transition of photo-responsive monolayer by UV and Vis irradiation: (■) CA on a n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified rough surface; (●) CA on a n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified flat surface; (▲) CA on a n-C_4H_9SH-CF_3AzoSH-SAM modified rough surface. (b) The shapes of water drops on a n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified rough surface upon UV and Vis irradiation.

In contrast to wettability of the surface anchored molecular shuttle, a n-C_4H_9SH-CF_3AzoSH-SAMs modified rough surface was found to change its wettability oppositely, from 140 ± 2 to 125 ± 2° as a result of UV/visible irradiation. This phenomenon is caused by the change in the dipole moment of the azobenzene molecules upon *trans* to *cis* photoisomerization *via* UV/visible irradiation.[7] In addition, we also pre-assembled a SAM of n-C_4H_9SH–CF_3AzoSH on rough gold surface under similar conditions and measured a CA of 140°, as shown in Fig. 2(a). For this SAM, even after 24 h immersion in α-CD solution, there is no change of the CA of the modified substrate, indicating that it is not easy for the hydrophilic α-CD to incorporate into the hydrophobic CF_3AzoSH-SAMs. These control experiments provide further evidence that the photo-induced up-down movement of α-CD in CF_3AzoSH-SAMs on gold substrates is the reason for the significant CA change under UV/visible irradiation.

To further confirm the photocontrolled molecular motion of α-CD/CF_3AzoSH-SAMs on gold, cyclic voltammetry (CV) was employed using the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system as a redox probe. Fig. 3(a) shows the cyclic voltammetric responses of the bare, n-C_4H_9SH-SAM and n-C_4H_9SH-α-CD/CF_3-AzoSH-SAM modified gold electrode in the presence of $Fe(CN)_6^{3-}$, as shown in Fig. 3(a), A–C, respectively. As reported, $[Fe(CN)_6]^{3-}$ can sterically not permeate through the β-cyclodextrin cavity,[10] so the permeability of $Fe(CN)_6^{3-}$ through the intermolecular voids should be considered. In the case of a n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified gold electrode, a pair of reversible waves (Fig. 3a-C) at a scan rate of 0.10 V s^{-1} should be due to many voids between the molecules of the α-CD/CF_3AzoSH-SAM modified gold electrode (Fig. S8†). Fig. 3a-D shows the cyclic voltammogram of n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified gold electrode irradiated for 20 min by UV light at 365 nm. Upon UV irradiation, we observed a rapid decrease in the current response, indicating that the SAMs partly inhibit the electron-transfer process between the probe and the gold electrode because of reduced number of voids after the up-to-down motion of α-CD (Fig. S8†). The switching of the anodic peak current of n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified gold electrode upon UV/visible irradiation is shown in Fig. 3b-A.

By comparison, we also studied the ion permeability of a n-C_4H_9SH-CF_3AzoSH-SAM modified gold electrode (Fig. S6†). Fig. 3b-B shows the switching of the anodic peak current of n-C_4H_9SH-CF_3AzoSH-SAM modified gold electrodes in the presence of $Fe(CN)_6^{3-}$ upon UV/visible irradiation. As demonstrated in Fig. 3b–B, the ion permeability barrier of n-C_4H_9SH–CF_3-AzoSH-SAM modified gold electrode changes very little upon the

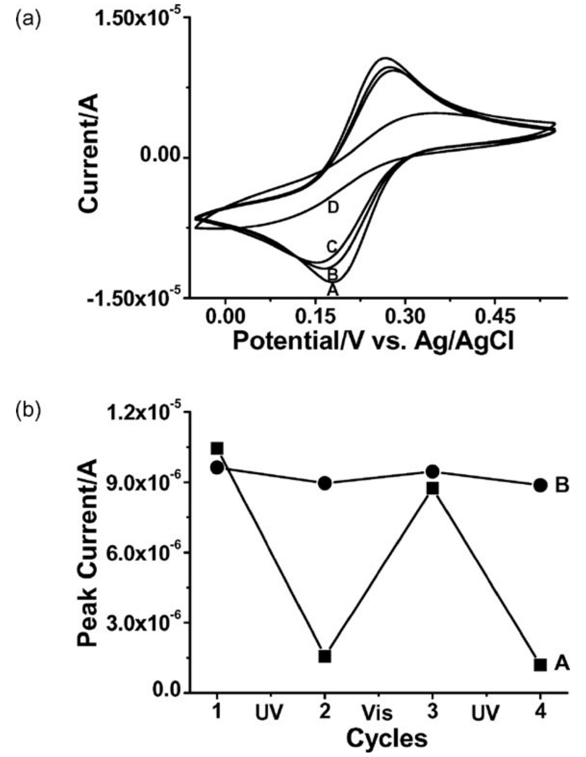

Fig. 3 (a) Cyclic voltammograms of (A) bare gold electrode, (B) n-C_4H_9SH-SAM modified gold electrode, (C) n-C_4H_9SH-α-CD/CF_3-AzoSH-SAM modified gold electrode, (D) n-C_4H_9SH-α-CD/CF_3-AzoSH-SAM modified gold electrode irradiated by UV light at 365 nm. The CV measurement was carried out in a solution of 2 mM $K_3[Fe(CN)_6]$ + 0.1 M KCl at a scan rate of 0.10 V s^{-1}. (b) Switching of the anodic peak current upon UV/visible irradiation: (■) peak current on a n-C_4H_9SH-α-CD/CF_3AzoSH-SAM modified gold electrode; (●) peak current on a n-C_4H_9SH-CF_3AzoSH-SAM modified gold electrode.

trans to *cis* photoisomerization of the azobenzene molecules *via* UV irradiation compared to that from the up-to-down motion of α-CD. Therefore, the CV data confirm the photocontrolled up-down motion of α-CD in CF_3AzoSH-SAMs on gold surfaces.

In conclusion, we have designed and constructed a photocontrolled molecular shuttle SAM based on α-CD and azobenzene on gold surfaces, which can reversibly switch the surface wettability by transferring external energy (light) to molecular mechanical motion, leading to altering the surface wettability. The surface wettability switches uncommonly from hydrophilicity to hydrophobicity under UV irradiation compared to the traditional wettability change from the photoisomerization of *trans*- to *cis*-azobenzene monolayers under UV irradiation. As mentioned, the photocontrolled change from hydrophilicity to hydrophobicity is fast, however, the reversed change is slow which needs to be further improved. In addition, such a line of research may provide ways to visualize the microscopic molecular motion by observing the change of a macroscopic property.

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