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Pesticide Macroscopic Recognition by a Naphthol-Appended Calix[4]arene

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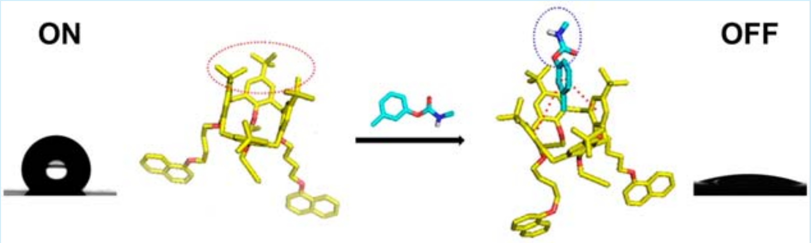
Supporting Information



ABSTRACT: A new naphthol-appended calix[4]arene (NOC4) has been synthesized and characterized. NOC4 is clicked onto a microstructured Au surface and exhibits selective macroscopic recognition of metolcarb (MC) via contact angle measurements. The proposed wettability sensing device displays remarkable specificity and is fast and easy to use, which should be suitable for the rapid detection of MC in environmental monitoring.

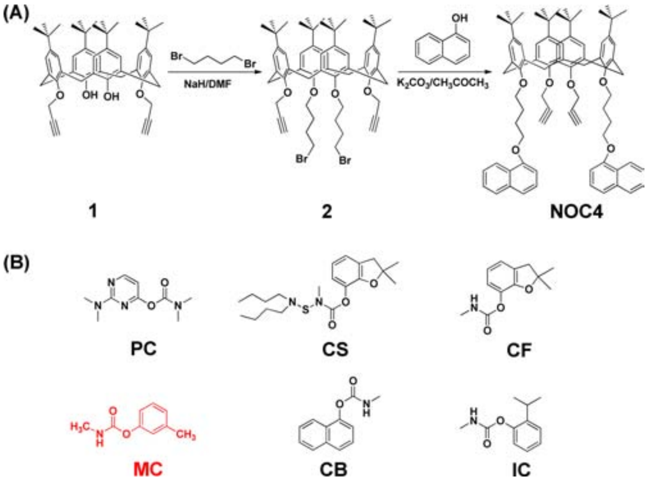
The widespread use of pesticides poses a potential hazard to the environment and human health.[1−3] Detection of pesticides can be undertaken using a variety of techniques including high performance liquid chromatography (HPLC), gas chromatography (GC), or NMR spectroscopy.[4,5] However, these techniques require the pesticides to be in the solution phase and a high level of operator experience and are inconvenient to use for on-site detection outside of the laboratory. Therefore, the development of a simple, rapid, and visual method for pesticide recognition remains a challenging task.

The wetting behavior of droplets on a surface can be analyzed by examining the contact angle of the droplets.[6,7] The contact angle (CA) is a function of the hydrophobic and hydrophilic forces at the interface of the droplet and the surface. Such contact angles are macroscopic in size and can be visualized directly.[8,9] Thus, to resolve the challenging task of on-site and fast detection, we designed a new strategy to introduce host−guest chemistry onto surfaces for the visual detection of pesticides. Calix[*n*]arenes, as third generation hosts, are an ideal molecular platform for fabricating responsive surfaces, because their cavities are adjustable by varying their shape and size.[10,11] Just recently, we reported a fluorescent calix[4]arene-modified silicon surface to recognize tryptophan by a fluorescent and wettable dual signal.[12] To our knowledge, the visual method for pesticide recognition on the surface is unexplored.

Herein, we report the synthesis of a new naphthol-appended calix[4]arene (NOC4) which has been successfully applied to a functional microstructured Au surface using a simple click reaction.[13] The NOC4 surface can act as a convenient and effective macroscopic sensor for the recognition of metolcarb (MC). In addition, the wettability sensor should be suitable for the production of MC recognition chips that can be used in environmental monitoring.[14]

The synthetic strategy toward NOC4 is depicted in Scheme 1. NOC4 was synthesized in two steps: first, calix[4]arene **1** (0.5 g) and NaH (0.14 g) were diluted in 20 mL of DMF, stirring for 30 min at room temperature. Then, 0.6 mL of 1,4-

Scheme 1. (A) Process Synthesis of Host NOC4; (B) Structure of Carbamate Pesticides



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dibromobutane was added to stir for 1 h. Evaporation of the solvent offered a crude product that was purified by column chromatography to give a white powder of calix[4]arene **2** (0.3 g, 72%). Second, calix[4]arene **2**, K_2CO_3 (0.09 g, 0.6 mmol), and 2-naphthol (0.1 g, 0.6 mmol) were diluted into 40 mL of CH_3COCH_3 to reflux for 10 h. After filtration and evaporation of the solvent, the solid residue was directly purified by a silica gel column to obtain target NOC4 in 95% yield.

The binding of NOC4 (10^{-5} M, CH_3CN) with various pesticides (0–10^{-5} M, CH_3CN) including metolcarb (MC), pirimicarb (PC), carbosulfan (CS), carbofuran (CF), carbaryl (CB), and isoprocarb (IC) was investigated by fluorescence spectroscopy (excitation wavelength = 265 nm). As shown in Figure 1, the fluorescent intensity of NOC4 was effectively increased when bound to MC in comparison with the other pesticides, indicating its high selectivity toward MC.

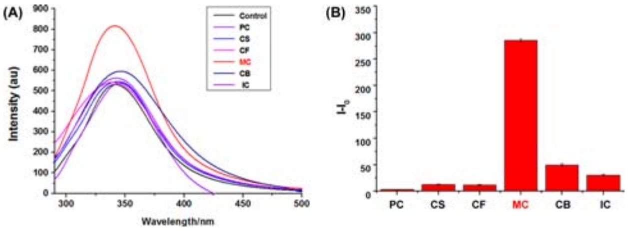

Figure 1. (A) Fluorescence intensity for mixture of NOC4 (10^{-5} M) and different pesticides in CH_3CN, indicating that NOC4 for metolcarb possess selective by fluorescent assay. (B) Histogram shows the fluorescence spectral intensity of different pesticides at 340 nm. More clearly, this also showed highly selective recognition for MC.

Furthermore, the fluorescence titration of NOC4 (10^{-5} M, CH_3CN) was conducted by the addition of MC in concentrations from 0 to 10^{-5} M. Thus, among the pesticides studied, only MC exhibited a significant change in fluorescence upon titration with NOC4 (Figure S6). In the Job plot, a maximum fluorescence change was observed when the molar fraction of NOC4 to MC was 0.5, indicative of the formation of a 1:1 host–guest complex (Figure S7). The association constant (K_a) for MC was calculated to be 1.2×10^5 M^{-1} using the Benesi–Hildebrand equation.

To further verify the binding between NOC4 and MC, the host–guest complex was analyzed using electrospray ionization mass spectrometry (ESI-MS). The molecular ion (m/z) peak of the intact host–guest complex $[NOC4 + MC]^+$ was observed at 1287.1 m/z (Figure S8). To confirm the interaction between NOC4 and MC, the host–guest complex was further analyzed by ^1H NMR. The resonances of the protons on the aromatic ring H_1 of NOC4 shifted downfield by 0.03 ppm upon the binding of MC. At the same time, the MC aromatic H_a proton and its methyl H_b proton undergo upfield shifts of 0.02 and 0.01 ppm, respectively, as shown in Figure 2. Moreover, ^1H NMR titration shows, with increasing concentrations of host NOC4, the MC aromatic H_a proton and its methyl H_b proton undergo upfield shifts of 0.07 and 0.09 ppm (Figure S9). These chemical shift changes of the NOC4 and MC proton resonances indicate that MC inserts into calix[4]arene upper rim.

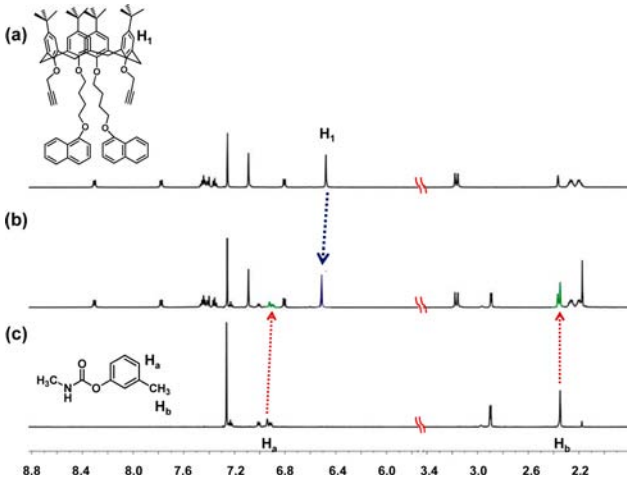

Figure 2. Partial ^1H NMR spectra ($CDCl_3$, 600 MHz, 298 K): (a) 8 mM NOC4; (b) 8 mM NOC4 + 8 mM MC; (c) 8 mM MC, which showed NOC4 can bind MC, selectively.

The interface mimics the surfaces of lotus leaves in order to amplify the output signal.[15] The self-assembled monolayers (SAMs) based on NOC4 were constructed by click reaction between the azide bonding microstructured Au interface. The contact angle of the Au interface was 37.8 ± 2.0°. After modification by azide and following the click reaction with NOC4, the functional interface was hydrophobic (128.1 ± 2.0°), shown in Figure 3. Moreover, electrochemical impedance spectroscopy (EIS) was also used to study the Au electrode. The EIS of the NOC4 SAMs (2294.2 Ω) was significantly increased, allowing the conclusion that the functional SAMs were successfully modified in the Au interface (Figure S12).

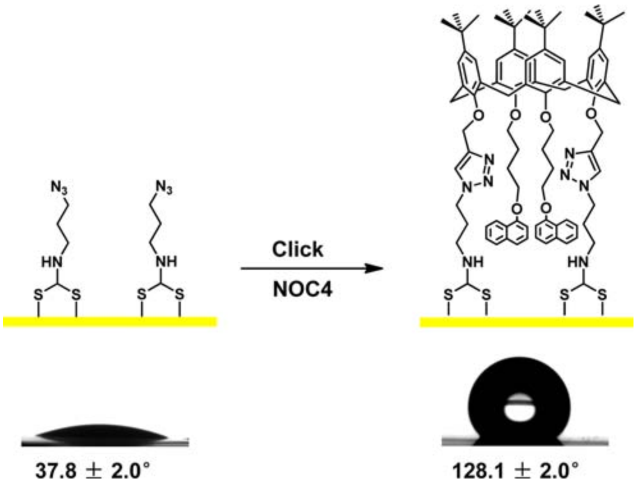

Figure 3. Self-assembled monolayers (SAMs) based on NOC4 were constructed by a click reaction between the azide bonding micro structured Au interface with CA, indicating that the NOC4-SAMs were constructed perfectly.

The contact angle (CA) signal was used to identify the interaction between the host and guest. Figure 4 shows the specific selectivity of NOC4 to MC. When MC is present the functional interface is hydrophilic (20.6 ± 2.0°), whereas for the other pesticides the interface appears hydrophobic. For these pesticides, the surface remains the same as the NOC4 assembled interface, for which the contact angle value is 128.1 ± 2.0°. This observation is consistent with the fluorescence data which indicates that NOC4 is highly selective toward MC. A cycling experiment also shows good reversibility for this

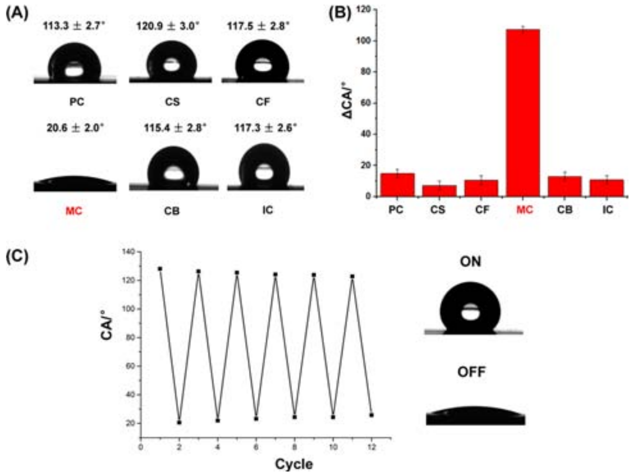

Figure 4. (A) Water-drop profiles on NOC4 SAMs. CA relationship images for the NOC4 SAM with different pesticides, which indicates the selective wettability responsiveness of NOC4 toward MC. (B) Histogram of CA relationship images of NOC4 with different pesticides, indicating NOC4 as practically useful in macroscopic recognition for metolcarb through contrast CA change. (C) Cycling experiment into the wettability switching behavior of the NOC4-modified surfaces with MC and water, which indicates good reversibility between superhydrophobicity and high hydrophilicity.

property, and this could allow a wide range of applications in a diverse range of fields (Figure 4c).

For quantitative analysis, EIS and contact angle measurements of NOC4 in the presence of different concentrations of MC were carried out (Figures S13−15). According to Figure S13, the concentration of MC ranges from 1×10^{-10} to 1×10^{-3} M, and the detection limit for MC was 1×10^{-7} M. Meanwhile, the concentration of MC ranges from 1×10^{-6} to 1×10^{-2} M along with the interface changing from hydrophobic to hydrophilic.

On the basis of these results, a cooperative molecular mechanism is proposed for MC macroscopic recognition (Figure 5). Initially, the tertiary butyl groups of NOC4 act to make the surface display hydrophobic behavior. Binding of MC into the cavity of NOC4 is stabilized through $\pi-\pi$ interactions. This MC binding leads to the surface changing to display hydrophilic behavior, because the MC induces the amide group which will hydrogen bond with water.

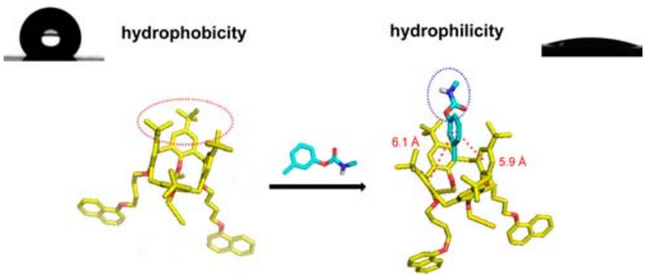

Figure 5. Proposed interactions between NOC4 bind MC, which indicates the cooperative molecular mechanism of NOC4 toward metolcarb.

In conclusion, a naphthol-appended calix[4]arene was successfully synthesized for a microstructured interface by click chemistry and characterized by NMR and ESI-MS. The NOC4 displays high selectivity for MC as shown by fluorescence, ESI-MS and ^{1}H NMR spectroscopy, and contact angle measurements. The results indicate that the wettability interface could be suitable in macroscopic recognition chips that can be used in environmental monitoring for the pesticide metolcarb.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, MS spectra, and XPS and ESI. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01075.

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Notes

The authors declare no competing financial interest.

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