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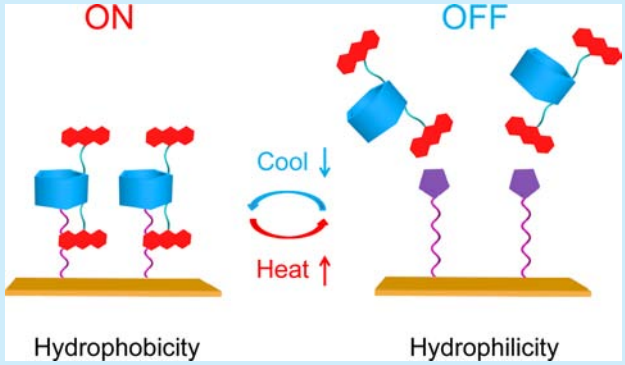
Temperature-Responsive Switch Constructed from an Anthracene-Functionalized Pillar[5]arene-Based Host–Guest System

Jiahai Bi,[†] Xiangfei Zeng,[†] Demei Tian, and Haibing Li*

Key Laboratory of Pesticide & Chemical Biology (CCNU), Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P.R. China

Supporting Information

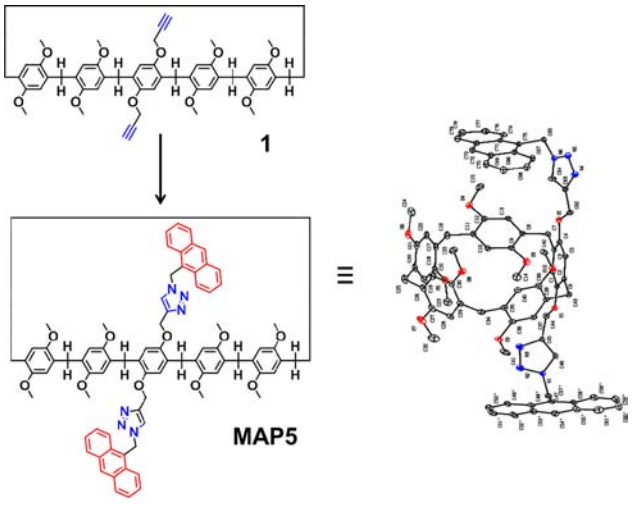
ABSTRACT: A monofunctionalized anthracene pillar[5]arene (MAP5) was designed and synthesized by a click reaction. MAP5 was bound to an ionic liquid through host–guest interactions to modify a gold interface. The bonding and release of MAP5 was readily and reversibly controlled by temperature regulation. The developed temperature-responsive switch at an interface can be used in memory storage, drug delivery, and sensing.



Stimuli-responsive host–guest systems have attracted much interest because of their application in a broad range of fields such as memory storage, drug delivery systems, sensors, and functional nanodevices.[1] Numerous external stimuli such as heat, pH, redox, and light have been utilized in these systems.[2] Thermal stimulation is of special interest because it can work rapidly, cheaply, and cleanly and is readily available. Thermally responsive systems have a wide range of specific uses in controlled drug delivery,[3] smart surfaces,[4] biomaterials,[5] and mass separation.[6] For example, thermoresponsive polymers such as poly(*N*-isopropylacrylamide),[7] poly(vinyl methyl ether), and poly(2-ethyl-2-oxazoline) exhibit inverse phase behavior in solution. Most thermoresponsive systems have been studied in solution; thermally responsive interface systems are largely unexplored even though they could be widely applied in heat transfer, drug separation and transfer, and microfluidics.[8]

To develop a new thermoresponsive interface system, here we propose a new strategy involving host–guest interaction on a surface. Pillar[*n*]arenes (n = 5–10), composed of hydroquinone units linked by methylene bridges at the *para* positions, are rigid and soluble in organic solvents, and the hydroquinone units can be conveniently functionalized with various substituents. The unique structure and easy functionalization of pillararenes afford them with outstanding ability to selectively bind different kinds of guests and act as a useful host platform to construct supramolecular surfaces.[9] For instance, Huang et al.[10] reported a pillar[5]arene–ionic liquid (IL) host–guest system that opened a new avenue to construct thermoresponsive systems. We considered that its rigid electron-rich cavity makes pillar[5]arene a good candidate as a host molecule for various electron-deficient guests. Therefore, here we design and synthesize a new pillar[5]arene with fluorescent anthracene groups by a click reaction (Scheme 1). We also modify a gold (Au) interface with an imidazolium IL to act as a thermoresponsive interface switch with the pillar[5]-arene. For the host–guest interaction between the developed monofunctionalized anthracene pillar[5]arene (MAP5) and IL, MAP5 is attached to an Au interface through thiol–Au self-assembly. When MAP5 bonds to an IL–surface-modifying

Scheme 1. Synthetic Strategy and Crystal Structure To Prepare Monofunctionalized Anthracene Pillar[5]arene (MAP5)



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additive surface at room temperature, the pillar[5]arene is pulled out from the IL with increasing temperature. The current can be recovered by controlling the temperature (Figure 1), so the system shows good switchable temperature-

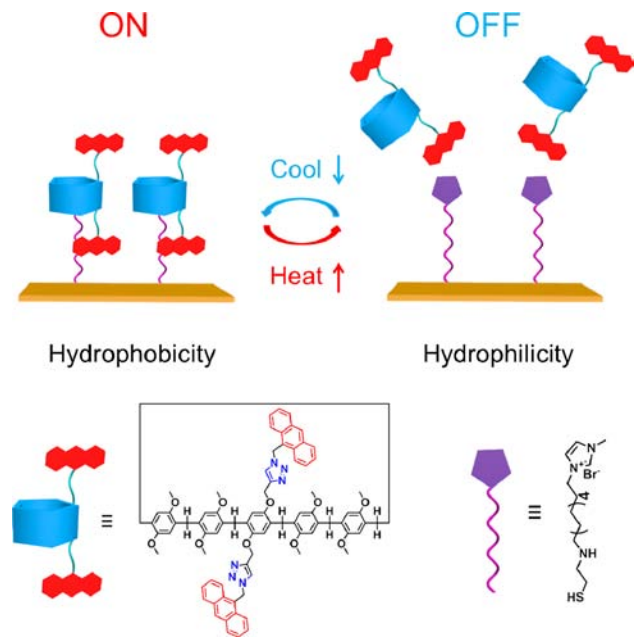

Figure 1. Schematic diagram of a temperature-responsive switch constructed using an anthracene-functionalized pillar[5]arene-based host–guest interaction.

responsive properties. This interface system based on the thermal response of a host–guest interaction is attractive for use in thermoresponsive memory storage, drug delivery systems, and sensors.

MAP5 with fluorescent groups was synthesized as outlined in Scheme 1. MAP5 was synthesized by click reaction of monofunctional pillar[5]arene **1** (300 mg, 0.376 mmol), azide anthracene (87.6 mg, 0.376 mmol), sodium ascorbate (68.2 mg, 0.376 mmol), and copper(II) sulfate pentahydrate (94 mg, 0.376 mmol) in 20 mL DMF overnight at 80 °C. When the reaction was completed, 20 mL of H_2O was added, and the mixture was extracted three times with ethyl acetate. The organic phase was washed with saturated brine and dried by anhydrous $MgSO_4$. The product was purified by column chromatography to obtain 390 mg of yellow solid, yield 82%. The structure of MAP5 was characterized by ^1H NMR spectroscopy (Figure S5), ^{13}C NMR spectroscopy (Figure S6), and MS (Figure S7). Single-crystal X-ray analysis (Scheme 1) confirmed the formation of MAP5. Crystals of MAP5 suitable for X-ray analysis were grown by slow evaporation of a solution of MAP5 in dichloromethane and methanol.

The rigid electron-rich cavity of pillar[5]arenes makes them good candidates as host molecules for various electron-deficient guests or other neutral molecules such as viologen derivatives, bis-imidazolium cations, *n*-hexane, alkanediamines, *n*-octyltrimethylammonium, and neutral bis(imidazole) derivatives.[7] It has been reported that pillar[5]arenes can also bond to ILs, so we designed an imidazolium with thiol groups(IL). To study the interaction between MAP5 and the IL, ^1H NMR measurements were performed. The ^1H NMR spectra showed that protons H_a, H_b, and H_c of the IL shifted upfield in the presence of MAP5; this indicates that MAP5 interacts with the IL (Figure 2). Computer simulation revealed that the formation of a complex between MAP5 and the IL was energetically favorable (Figure S13).

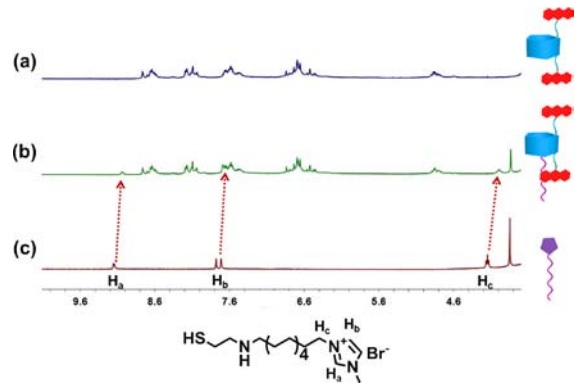

Figure 2. Partial ^1H NMR spectra (DMSO, 400 MHz) of (a) 8 mM MAP5; (b) 8 mM MAP5 + 8 mM IL; (c) 8 mM IL. The resonances of the protons on the imidazole ring of the IL H_a and H_b shifted upfield by 0.11 and 0.10 ppm, respectively, upon the binding of MAP5. At the same time, H_c of the IL exhibited an upfield shift of 0.15 ppm, showing that MAP5 could bind to the IL at 298 K.

Then, the binding of MAP5 with the IL was investigated by fluorescence spectroscopy. As shown in Figure 3, the

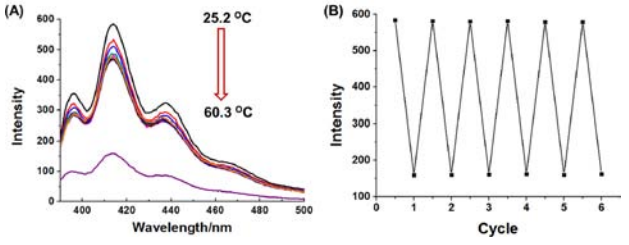

Figure 3. (A) Changes of fluorescence intensity with temperatures of 25.2, 28.8, 32.2, 36.5, 40.7, 44.1, 48.3, 51.8, 54.6, 55.9, 57.3, 59.1, and 60.3 °C, indicating the ionic liquid was released from the cavity of the pillar[5]arene at room temperature as the temperature gradually increased. (B) Cyclic changes in fluorescence with temperature variation, revealing the high temperature sensitivity of the system.

fluorescent intensity of MAP5 increased markedly with increasing temperature until 60 °C, when the fluorescence intensity sharply decreased. The fluorescence intensity recovered as the temperature was lowered. The fluorescence experiments show that temperature has a strong influence on the host–guest interaction in the system. We have been determined the variation of fluorescence intensity of the MAP5/IL host–guest system with temperature, but we found the intensity to be temperature independent. At the same time, the association constant (K_a) for MAP5/IL was calculated to be 2.6×10^4 M^{-1} using the Benesi–Hildebrand equation, which indicates that MAP5 readily interacts with the IL (Figure S9).

To study the mechanism of host–guest interactions in the MAP5/IL system, ^1H NMR measurements were performed at different temperatures. The resonances of the protons on the imidazole ring of the IL, H_b, and H_c, shifted downfield by 0.15 and 0.06 ppm with increasing temperature, respectively (Figure 4). This indicates that the IL is bound in the cavity of MAP5 at room temperature and is then released from the cavity of MAP5 as the temperature is inceased.

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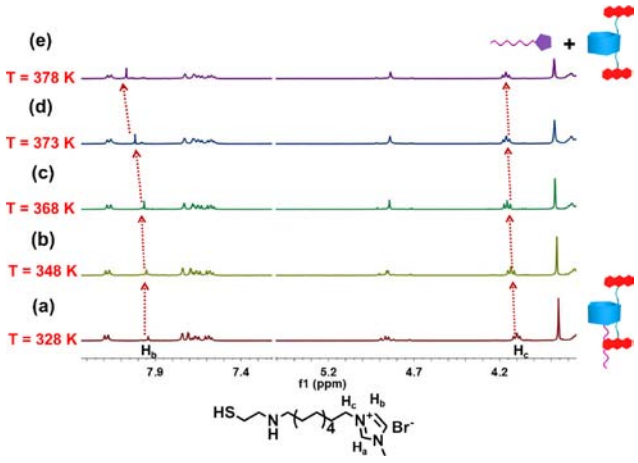

Figure 4. Partial ^{1}H NMR spectra of host and guest at temperatures of (a) 328 K; (b) 348 K; (c) 368 K; (d) 373 K; (e) 378 K. The spectra indicate that the ionic liquid was bound in the cavity of the pillar[5]arene at room temperature and was released at high temperature.

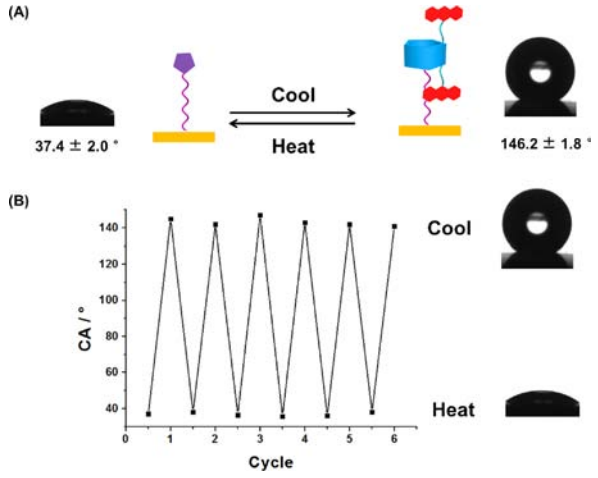

Figure 5. (A) Binding model of pillar[5]arene and ionic liquid on the an Au surface at room (left) and high (right) temperature. (B) Cycling experiment of the wettability switching behavior of IL-modified Au surfaces with MAP5 and water. Good reversibility between binding and release of the ionic liquid is obtained by temperature regulation.

The fluorescent quenching thermoresponsive mechanisms of MAP5 and IL were comprehensively investigated by theoretical calculations. At room temperature, the binding of MAP5 with IL formed compact species, which restricted the motions of the anthracene unit in the IL. The electron-deficient IL forces the anthracene unit to move closer to MAP5, limiting the rotation of the anthracene unit because of the steric crowding between MAP5 and the IL. These results confirm that formation of a host−guest complex between MAP5 and the IL decreases the fluorescence of MAP5 by restricting the rotation of the anthracene unit. Meanwhile, the fluorescence intensity of the bound IL was dramatically enhanced. With decreasing temperature, the IL was released from MAP5, and the anthracene unit of MAP5 was able to freely rotate, allowing the fluorescence of MAP5 to recover.

Wettability switches have attracted considerable attention because of their potential application in lab-on-a-chip devices, smart surface systems, and material harvesting. In general, self-assembled monolayers (SAMs) on controllable surfaces can switch reversibly between two stable states upon molecular stimulation because of their inherent physicochemical properties under specific environmental conditions. Therefore, we constructed a structured Au interface because the rough Au surface can amplify the output wettability signal (Figure 5). First, the Au surface was washed with acetone, ethanol, and water and then dried under nitrogen. The cleaned Au surface was soaked in a solution of 10^{-3} M IL for 2 h. The contact angle (CA) of the Au interface before modification was 132.4 ± 2.3° but decreased to 37.4 ± 2.0° following IL modification. That is, the Au interface changes from hydrophobic to hydrophilic, which indicates that a SAM of IL had been constructed. X-ray photoelectron spectroscopy (XPS) is another method used to characterize interfaces. Figure S6 reveals that after modification with IL the Au surface contained nitrogen and sulfur. This confirms that the Au interface was modified with IL.

The IL-modified Au surface was hydrophilic. The IL-modified Au surface was immersed in a solution of MAP5 for 2 h and washed with organic solvents. The measured CA of the MAP5-bound IL-modified Au interface was 146.2 ± 1.8°, revealing that the modified Au interface was super-hydrophobic. This indicates that MAP5 bound to the IL. Upon heating, the modified Au interface became highly hydrophilic.

On the basis of these results, a cooperative molecular mechanism is proposed for MAP5 binding to the IL (Figure 6).

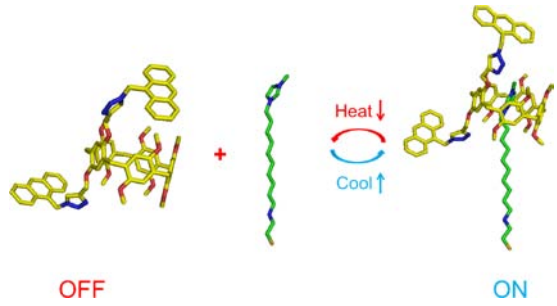

Figure 6. Model of the interaction between the pillar[5]arene and ionic liquid at room (left) and high (right) temperature.

MAP5 possesses a rigid electron-rich cavity that makes it a suitable host for an electron-deficient IL guest. Binding of the IL in the cavity of MAP5 is stabilized through electrostatic interactions at room temperature, including C−H···π and C−H···O hydrogen-bonding interactions. The fluorescence intensity of the Au interface increased when MAP5 was bound to the IL. With increasing temperature, MAP5 was released from the IL, which quenched the fluorescence intensity in solution. Meanwhile, when MAP5 was bound to the IL on the Au interface, the interface was hydrophobic. Upon heating, the Au interface turned hydrophilic as MAP5 was released.

In conclusion, a monofunctionalized anthracene pillar[5]-arene was synthesized and then characterized by NMR spectroscopy, ESI-MS, and single-crystal X-ray diffraction. The host−guest interaction between MAP5 and the IL was confirmed by ^{1}H NMR and fluorescence measurements. ^{1}H NMR spectroscopy and CA measurements revealed that the MAP5/IL host−guest system was responsive to temperature. A temperature-responsive switch was designed on the basis of an Au interface modified with MAP5 and IL. The interface system based on the thermoresponsive host−guest interaction between

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MAP5 and an IL may be applied in memory storage, drug delivery systems, and sensors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00097.

Experimental details, MS spectra, and XPS (PDF)

X-ray crystallographic data for MAP5 (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lhbing@mail.ccnu.edu.cn.

Author Contributions

†J.B. and X.Z. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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