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Obvious Vapochromic Color Changes of a Pillar[6]arene Containing One Benzoquinone Unit with a Mechanochromic Change Before Vapor Exposure

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We developed a color changeable aromatic vapor detection system by combining the mechanochromism and vapochromism of pillar[6]arene containing one benzoquinone unit. The pillar[6]arene solid color was changed by mechanochromism before vapor exposure. Different aromatic vapors then induced an obvious vapochromic color change from dark red to light orange or vice versa.

Chromism is a color change in the solid state caused by an external stimulus, such as vapochromism using vapor or mechanochromism using a mechanical force.¹ Vapochromism has recently attracted much attention because it can be applied to detect volatile organic compounds using color changes of solids observed with the naked eye.²⁻¹⁸

Pillar[n]arenes, which were first reported by our group in 2008,¹⁹ are pillar-shaped macrocyclic host molecules.²⁰⁻²³ Recently, we reported solid-state host-guest complexation of pillar[n]arenes. After heating to remove the solvent, activated pillar[5]arene crystals **1** (Fig. 1a) were able to quantitatively take up linear alkane vapors.²⁴ The solid-state molecular recognition of pillar[5]arenes was related to the host-guest chemistry of pillar[n]arenes.²⁵ Because the cavity size of pillar[5]arene was suitably sized for linear alkanes at approximately 4.7 Å, we observed uptake of linear alkane vapors as a guest by the activated pillar[5]arene crystals **1**. However, the pillar[5]arene crystals **1** were white and did not change color even after guest vapor uptake. To visually confirm guest vapor uptake by the naked eye, it is necessary to

introduce “tags” that induce a color change on guest vapor exposure. Therefore, we decided to introduce a benzoquinone moiety **2** as a tag to visualize uptake of the linear alkane guest vapor (Fig. 1a).²⁶ The benzoquinone group in **2** exhibits a charge-transfer (CT) interaction with the other 1,4-diethoxybenzene units in **2**. Because of the CT interaction, the activated crystals **2** were brown. A color change from brown to red was observed when the activated crystals **2** were exposed to the linear alkane guest vapor. Guest vapor uptake induced a crystal state transformation, which resulted in π - π stacking change between the benzoquinone and 1,4-diethoxybenzene groups. Unfortunately, the cavity of pillar[5]arene only fits linear alkane guests and does not fit bulky molecules. Thus, detection of vapors of bulky molecules, including branched alkanes, cyclic alkanes and aromatics, is difficult. In this study, we investigated the use of pillar[6]arene, which has larger cavity (ca. 6.7 Å) than that of pillar[5]arene (ca. 4.7 Å). Because of the larger cavity, activated pillar[6]arene crystals can take up vapors of branched alkanes, cyclic alkanes, and aromatic compounds.²⁷⁻³⁰ To introduce a tag, we synthesized pillar[6]arene with one benzoquinone unit **3** (Fig. 1b). Activated solid of **3** showed vapochromism on exposure to vapors of various aromatic guests. Furthermore, we discovered that the activated pillar[6]arene solid **3** exhibited mechanochromism. To the best of our knowledge, this is first example of dual-stimuli responsive chromic materials prepared from pillar[n]arenes.^{31, 32} Mechanochromism can be used to change the initial color of the solid before exposure of the activated solid **3** to aromatic vapors. By combining the vapochromism and mechanochromism, we were able to develop a vapochromic system that could indicate the presence of various aromatic vapors with an obvious color change.

Pillar[6]arene **3** was synthesized by oxidation of pillar[6]arene with 12 ethyl groups.³³ Activated solids were prepared by drying a solution of **3** in dichloromethane. Drying solid **3** at 80 °C under reduced pressure for 24 h was sufficient to de-solvate all dichloromethane molecules and afforded activated solid **3**. The activation was confirmed by ¹H NMR (ESI,

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Electronic Supplementary Information (ESI) available: Experimental section, powder X-ray diffraction patterns, FT-IR, DSC, ¹H NMR and diffuse reflectance spectroscopy. See DOI: 10.1039/x0xx00000x

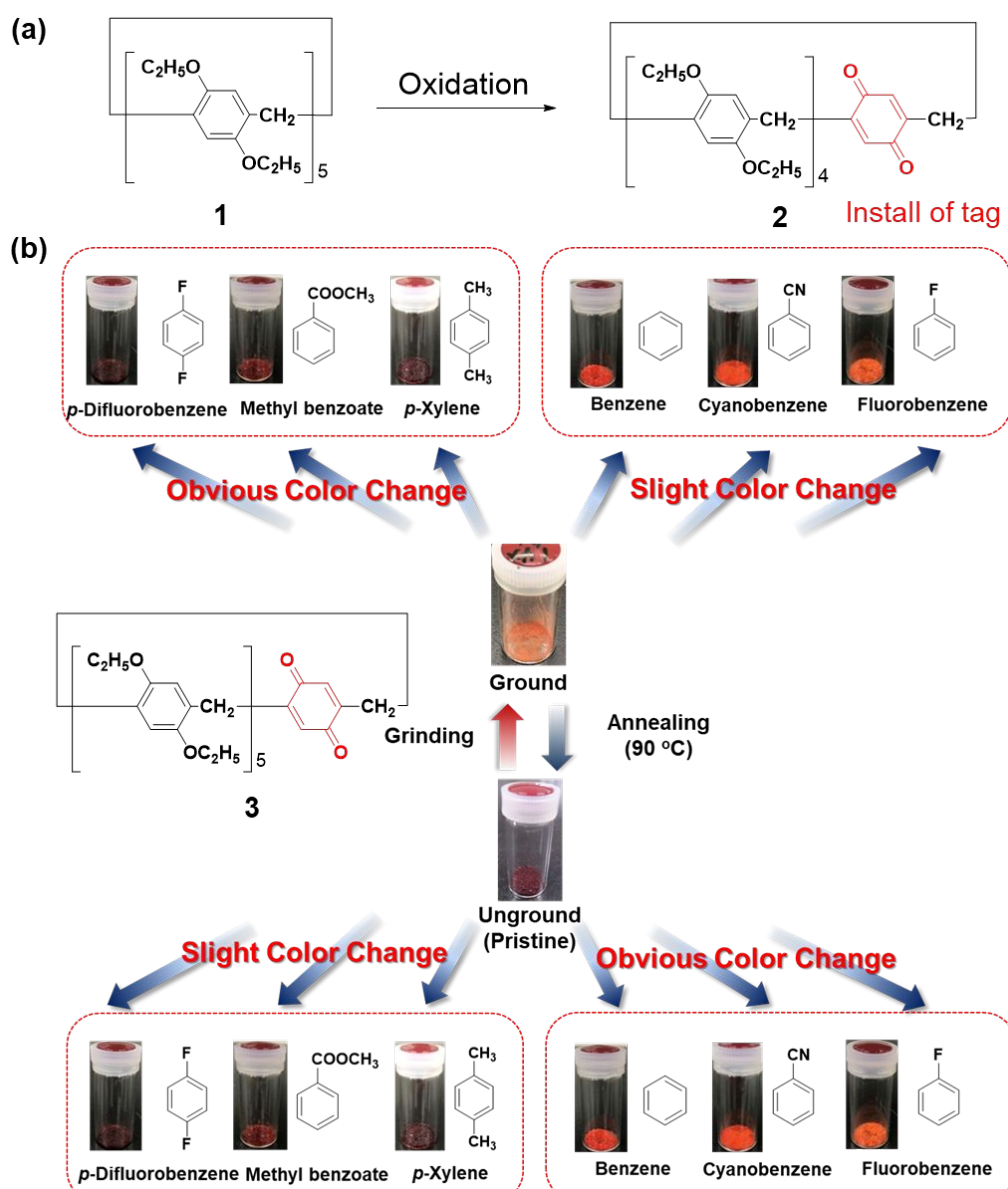


Fig. 1 (a) Chemical structures of pillar[5]arenes bearing 10 ethyl groups **1** and containing one benzoquinone unit **2**. (b) An obvious vapochromic color change obtained by combination of the vapochromic and mechanochromic behavior of pillar[6]arene containing one benzoquinone unit **3**.

Fig. S1). When the activated solid **3** was ground in an agate mortar, it showed mechanochromism with a color change from dark red to light orange (**Fig. 1b**). This color change was monitored by diffuse reflectance spectroscopy (**Fig. 2**). Absorption of the activated solid **3** was mainly observed at 500 - 700 nm (**Fig. 2a**). After grinding, the absorption intensity at 500 - 700 nm decreased (**Fig. 2b**), which would result in the color change. To understand the mechanochromic behavior, we performed powder X-ray diffraction (PXRD) measurements. Both the ground and unground (pristine) solids **3** were amorphous (**Fig. S2**), which showed that the mechanochromism was not induced by a crystal transformation. Next, we performed FT-IR measurements. After grinding, the peak derived from C=O stretching shifted from 1650 to 1652 cm^{-1}

1 (**Fig. S3**), indicating that grinding caused a change in the CT interaction between the benzoquinone and 1,4-diethoxybenzene moieties. This change in the CT interaction would cause the color change.

The color of ground solid **3** could revert to that of the pristine state on heating. When ground solid **3** was heated at 90 °C for 3 h, the color changed from light orange to the dark red of the pristine solid. The diffuse reflectance spectrum after heating (**Fig. 2c**) was almost the same as that of the pristine solid **3** (**Fig. 2a**). During the heating process, melting of **3** was observed at 60 °C by DSC measurements (**Fig. S4**). Thus, we concluded that the reversal of the color change occurred when the CT interaction was re-established on melting.

Subsequently, we investigated vapochromism using ground and pristine solids **3**. Pristine solid **3** prepared without grinding was exposed to guest vapors of *p*-difluorobenzene, methyl benzoate, *p*-xylene, benzene, cyanobenzene, and fluorobenzene. These vapors were taken up by solid **3**, which were confirmed by ^1H NMR measurements (**Figs. S5-S10**). The

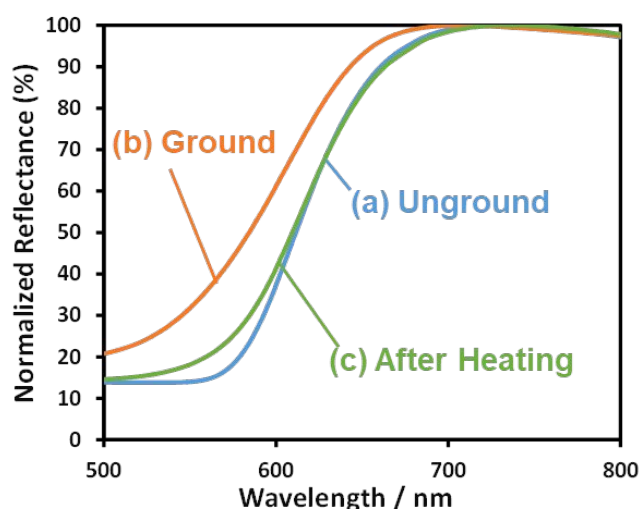


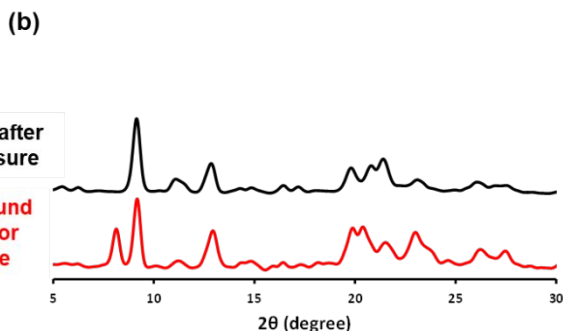
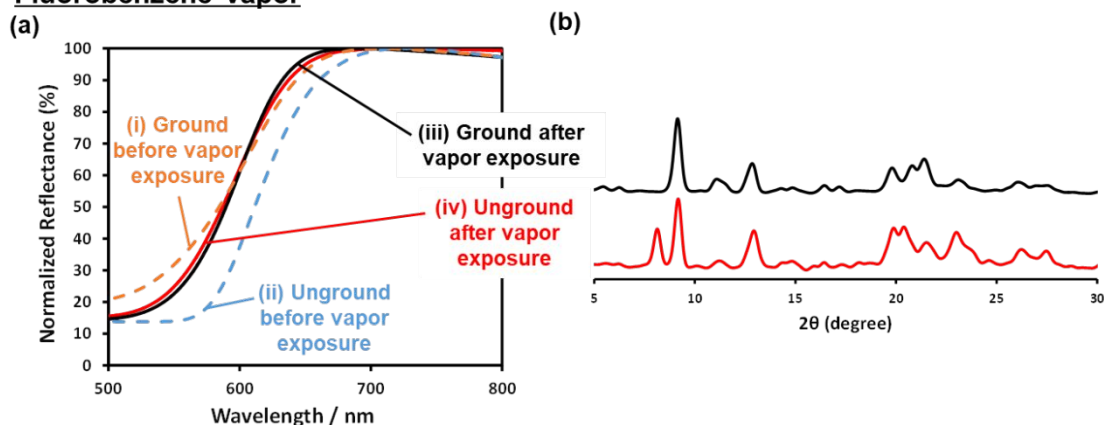
Fig. 2 Diffuse reflectance spectra of ground (b, orange line) and unground (pristine) solids **3** (a, blue line) and ground solid **3** after heating (c, green line).

time taken to reach the equilibrium state depended on the kind of vapor (**Figs. S5-S10**). The color changes on vapor uptake was investigated (**Fig. 1b**). Pristine solid **3** was dark red, and it showed an obvious color change to light orange upon exposure

to guest vapors of benzene, cyanobenzene, and fluorobenzene. By contrast, there was no obvious color change of pristine solid **3** on exposure to *p*-difluorobenzene, methyl benzoate, and *p*-xylene vapors and it stayed dark red after uptake of these guest vapors. Because solid **3** exhibited mechanochromism, guest vapor uptake was also investigated using ground solid **3**. The color of ground solid **3** was light orange. An obvious clear color change from light orange to dark red was observed after exposure to *p*-difluorobenzene, methyl benzoate, and *p*-xylene vapors. By contrast, ground solid **3** did not show an obvious color change when exposed to benzene, cyanobenzene, and fluorobenzene vapors and it remained close to the original light orange color. In summary, benzene, cyanobenzene, and fluorobenzene vapors could be detected using ground solid **3** with a color change from light orange to dark red, and *p*-difluorobenzene, methyl benzoate, and *p*-xylene vapors could be detected by pristine solid **3** with color change from dark red to light orange. Combining the vapochromism and mechanochromism of solid **3** provides a vapor detection system with obvious color changes.

To better understand this vapor detection system, PXRD, diffuse reflectance spectroscopy and FT-IR measurements were performed before and after uptake of these vapors using the

Fluorobenzene Vapor



p-Xylene Vapor

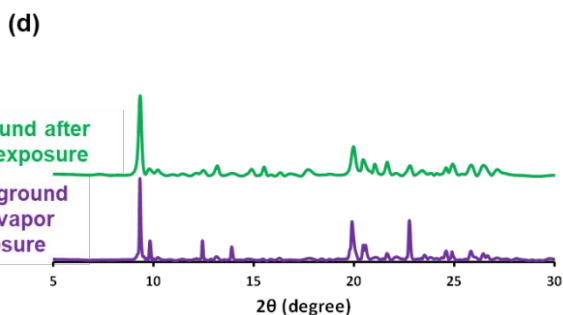
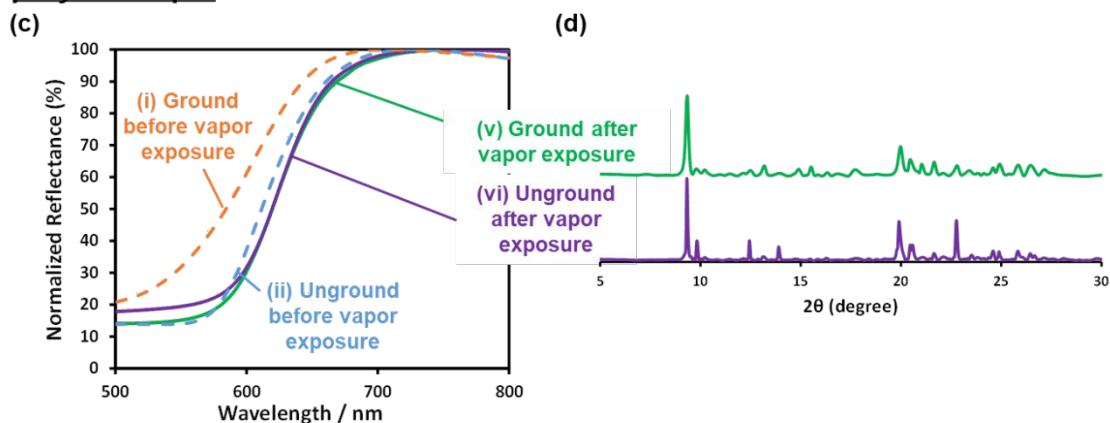


Fig. 3 (a and c) Diffuse reflectance spectra and (b and d) powder X-ray diffraction patterns. Ground (i, orange line) and unground solids **3** (ii, blue line) before vapor exposure. Ground (black lines, iii) and unground solids **3** (red lines, iv) after exposure to fluorobenzene vapor. Ground (green lines, v) and unground solids **3** (purple lines, vi) after exposure to *p*-xylene vapor.

ground and pristine solids **3** (**Figs. 3, S3, S11 and S12**). No PXRD patterns were observed for either of these solids **3** (**Fig. S2**), indicating they were in an amorphous state. By contrast, clear patterns were observed when unground solid **3** was exposed to

fluorobenzene vapor (Fig. 3b, red line). The same pattern was observed after exposure of ground solid **3** to fluorobenzene vapor (Fig. 3b, black line), indicating that the assembled state after the fluorobenzene vapor uptake was independent of the grinding. After exposure to fluorobenzene vapor, both the ground and pristine solids **3** were the same color (Fig. 3a, red and black lines), which indicated that the same solid **3** was obtained after exposure to fluorobenzene vapor whether the original solid was ground or not. After exposure of pristine solid **3** to *p*-xylene vapor (Figs. 3c,d, purple lines), the PXRD pattern and diffuse reflectance spectrum of solid **3** were the same as those of ground solid **3** after exposure to *p*-xylene vapor (Figs. 3c,d, green lines). Therefore, solids **3** reached the same state after exposure to vapors independently of the grinding. The same PXRD patterns and diffuse reflectance spectra of solid **3** were observed after exposure to other vapors (Figs. S11 and S12). We performed FT-IR measurements (Fig. S3). After uptake of these guest vapors, C=O stretching were broadening, indicating that the guest vapor uptake induced different CT interaction.

In conclusion, we developed an aromatic vapor detection system by combining the vapochromism and mechanochromism of pillar[6]arene solid **3**. The initial color of solid **3** could be changed using mechanochromism. Pristine solid **3** prepared without grinding was dark red, and ground solid **3** was light orange. Exposure of ground and pristine solids **3** to *p*-difluorobenzene, methyl benzoate and *p*-xylene vapors gave dark red solids. Therefore, an obvious color change would be observed if light orange ground solid **3** was used for detection of these vapors. By contrast, exposure to benzene, cyanobenzene, and fluorobenzene vapors gave a light orange solid. Therefore, an obvious color change would be observed if dark red unground solid **3** prepared was used to detect these vapors. This vapochromism and mechanochromism system provides a new direction for the design of vapochromic systems with obvious color changes.

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Conflicts of interest

There are no conflicts to declare.

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Table of Contents (TOC) Graphic

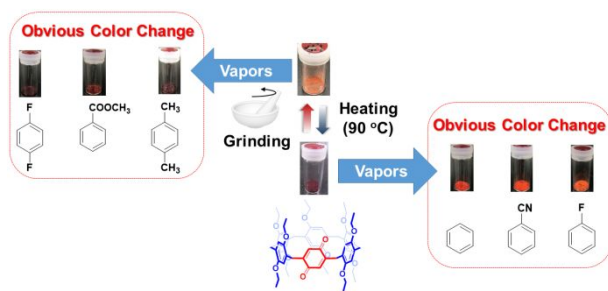
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By mechanochromism before vapor exposure, different aromatic vapors induced an obvious vapochromic color change.