

# Separation of Benzene and Cyclohexane by Nonporous Adaptive Crystals of a Hybrid[3]arene

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**ABSTRACT:** The separation of benzene and cyclohexane is one of the most challenging tasks in the petrochemical field. However, conventional separation methods suffer from cumbersome operation, huge energy expenditure, or use of entrainers. Herein, we develop an environmentally friendly and energy saving adsorptive separation strategy using nonporous adaptive crystals of a hybrid[3]arene (**1**). Adaptive **1** crystals separate benzene from an equimolar benzene/cyclohexane mixture with a purity of 97.5%. The selectivity comes from the stability and variability of the new crystal structure upon capture of the preferred guest, benzene. Moreover, reversible transformations between the nonporous guest-free structure and the guest-containing structure make **1** highly recyclable.

Over the past decades, the separation of benzene (Bz) and cyclohexane (Cy) is classified as one of the most challenging tasks in the chemical and petrochemical industries.<sup>1</sup> Bz, as a very important petrochemical product, is a generally identified volatile organic compound with tremendous industrial and environmental significance.<sup>2</sup> Cy is not only an important feedstock for varnishes, resins, and nylon fibers but also the raw material for producing cyclohexanol, caprolactam, cyclohexanone, etc.<sup>3</sup> In the chemical industry, Cy is mainly obtained from the catalytic hydrogenation of Bz.<sup>4</sup> It is of paramount importance to remove the unreacted Bz from the reactor's effluent stream for high-purity Cy. However, the separation of Bz from Cy is extremely difficult due to their similar physical properties.<sup>5</sup> The slight difference in boiling points (only 0.6 K) between Bz (353.25 K) and Cy (353.85 K) and azeotrope formation make them almost impossible to separate via a traditional distillation process. Currently, the dominant industrial methods for separation of Bz/Cy mixtures are extractive distillation and azeotropic distillation.<sup>6</sup> However, these options require high energy, accompanied by process complexity and high operating costs. Therefore, it is necessary and desirable to develop easy operation and more energy efficient methods to separate Bz and Cy.

By exploiting the differences of Bz and Cy in molecular sizes and geometries, adsorptive separation through ordered porous materials has been an efficient alternative separation method.<sup>7</sup> For example, metal–organic frameworks (MOFs) have been experimentally investigated for the adsorptive separation of Bz and Cy.<sup>8</sup> However, it is challenging in the design and synthesis of suitable MOFs because their molecular sizes are very close. Moreover, MOFs, constructed by reversible metal–ligand bonds, are not stable enough for practical recycling application.<sup>9</sup> Therefore, the development of new stable and recyclable adsorbents for efficient separation of Bz and Cy is urgently needed.

Recently, our group has demonstrated pillar[*n*]arene-based nonporous adaptive crystals (NACs) for separating hydro-

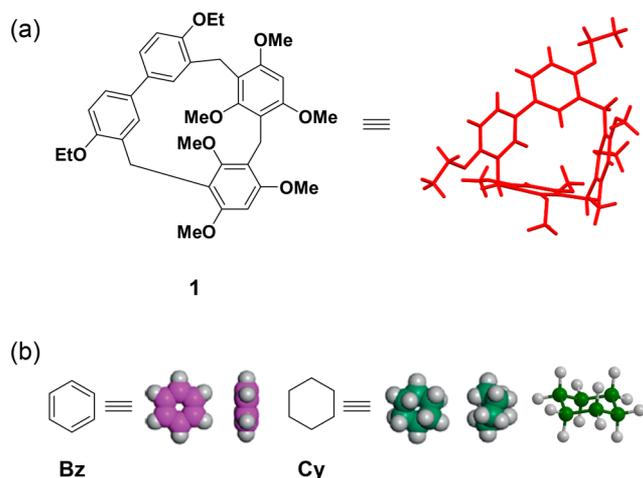
carbons with good performance.<sup>10,11</sup> NACs are nonporous in the initial crystalline state, but their intrinsic or extrinsic porosity can be induced by specific vaporized species through supramolecular interactions, thus generating voids to capture guest molecules. These unique characteristics make them a new class of adsorptive separation materials that function at the supramolecular level.<sup>12</sup> However, the separation of Bz and Cy cannot be achieved by nonporous adaptive perethylated pillar[5]arene or perethylated pillar[6]arene crystals.<sup>11c</sup> Herein, for the first time, we utilized nonporous hybrid[3]arene (**1**) crystals as adsorptive separation materials to realize the successful separation of Bz and Cy (Figure 1). We found adaptive **1** crystals separated Bz from a Bz/Cy equimolar mixture with a purity of 97.5%. The selectivity comes from the stability and change of the new crystal structure upon capture of the preferred guest. Furthermore, the adsorbed Bz was removed simply by heating, making these crystals recyclable without losing performance.

Hybrid[3]arene **1**, a novel macrocycle recently reported by us, was successfully synthesized by the one-step reaction of 4,4'-biphenol diethyl ether, 1,3,5-trimethoxybenzene, and paraformaldehyde in the presence of trifluoroacetic acid (TFA) as the catalyst (Scheme S1).<sup>13</sup> Activated crystalline **1** (**1α**) was recrystallized from acetone and dried under vacuum at 150 °C overnight. <sup>1</sup>H NMR (Figure S1) and thermogravimetric analyses (TGA, Figure S2) verified that the solvent was removed. As suggested by powder X-ray diffraction (PXRD, Figure S3), **1α** was crystalline. A N<sub>2</sub> sorption experiment showed **1α** was nonporous, with a BET surface area of 0.900 m<sup>2</sup>/g (Figure S4).

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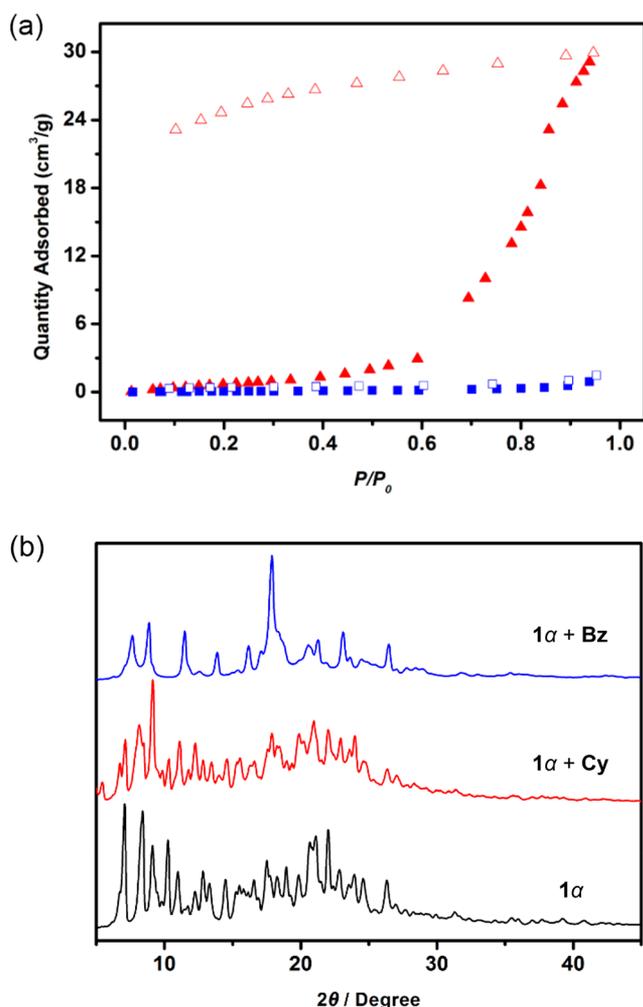
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**Figure 1.** Chemical structures: (a) hybrid[3]arene **1**; (b) benzene (Bz); and cyclohexane (Cy).

Despite its nonporous character, the capture capacity of **1 $\alpha$**  for Bz and Cy was evaluated by vapor sorption isotherms (Figure 2a). **1 $\alpha$**  took up Bz when the vapor pressure exceeded



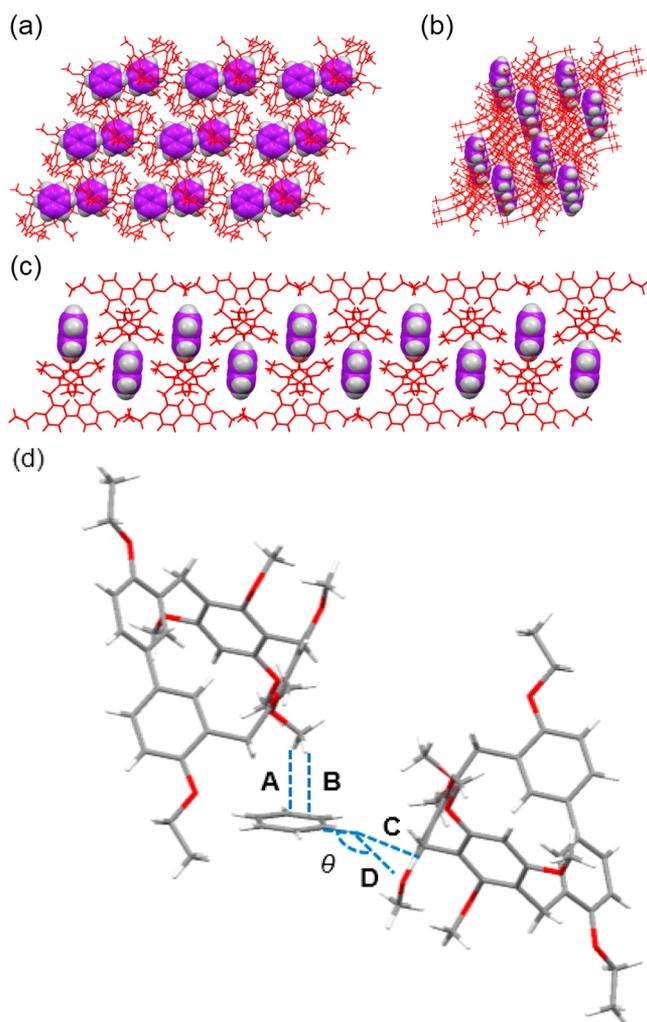
**Figure 2.** (a) Vapor sorption isotherms of **1 $\alpha$**  toward Bz (red triangles) and Cy (blue squares). Solid symbols: adsorption. Open symbols: desorption. (b) PXRD patterns of **1 $\alpha$**  after being exposed to Bz and Cy.

a certain value ( $P/P_0 = 0.6$ , Figure 2a, solid red triangles), suggesting a gate-opening behavior. However, **1 $\alpha$**  adsorbed a negligible amount of Cy even though  $P/P_0$  reached 1.0 (Figure 2a, solid blue squares). More interestingly, in the desorption process, only a small amount of adsorbed Bz in **1 $\alpha$**  was released at the beginning (Figure 2a, blank red triangles). The final adsorbed dose of Bz left in **1 $\alpha$**  was 23.1 cm<sup>3</sup>/g. In contrast, most Cy molecules were released under reduced pressure (Figure 2a, blank blue squares). These results suggested the stable storage of Bz in **1 $\alpha$** .

<sup>1</sup>H NMR spectra and TGA experiments were carried out to investigate the adsorption capacity of Bz and Cy in **1 $\alpha$** . As shown in Figure S9, **1 $\alpha$**  reached the saturation point after 10 h. The adsorption amount of Bz was about one Bz/**1** at saturation (Figure S7), while the uptake of Cy for **1 $\alpha$**  could be neglected (Figures S8 and S10). TGA of **1 $\alpha$**  showed a weight loss of 10.9% at 100 °C after adsorption of Bz vapor for 12 h, demonstrating that one **1** molecule contained one Bz molecule (Figure S11). However, there was nearly no weight loss of **1 $\alpha$**  before 200 °C after adsorption of Cy vapor for 12 h (Figure S12). These results showed that **1 $\alpha$**  captured Bz, but not Cy. The mechanism behind the uptake of Bz or Cy vapor was then investigated by PXRD experiments. Significantly, the PXRD pattern of **1 $\alpha$**  did not change after adsorption of Cy vapor but did change after capture of Bz vapor (Figure 2b), meaning that the formation of a new structure of **1** occurred after adsorption of Bz.

To reveal the mechanism of the adsorption of **1 $\alpha$** , single crystals of Bz@**1** were obtained by slow evaporation of a solution of **1** in Bz (Figure 3). In the Bz@**1** crystal structure, **1** became distorted. In addition, the distorted **1** molecules were arranged in infinite channels. Surprisingly, Bz molecules were not in the cavities of **1** molecules, but located in the self-assembled pores and sandwiched by two adjacent **1** molecules. The main driving forces came from multiple C–H $\cdots$  $\pi$  and C–H $\cdots$ O interactions (C–H $\cdots$  $\pi$  distances: 2.712 Å, 2.932 Å, 2.651 Å; C–H $\cdots$ O distance: 2.982 Å; Figures S14–S16). The selectivity of **1 $\alpha$**  for Bz was ascribed to the formation of a highly stable crystal structure after adsorption of the guest molecule.<sup>12b</sup> Additionally, the PXRD pattern of **1 $\alpha$**  after capture of Bz was consistent with that simulated from the crystal structure of Bz@**1**, indicating that the crystal structure transformed from **1 $\alpha$**  to Bz@**1** upon capture of Bz (Figure S13).

Based on the sorption ability, we wondered whether **1 $\alpha$**  could separate Bz/Cy mixtures. A time-dependent solid (**1 $\alpha$** )–vapor (from an equimolar Bz/Cy mixture) sorption experiment was carried out. As shown in Figure 4a, the adsorption amount of Bz in **1 $\alpha$**  increased with time. It took about 7 h to reach saturation. However, the adsorption amount of Cy in **1 $\alpha$**  was negligible. These results indicated that **1 $\alpha$**  adsorbed Bz with a high selectivity, but not Cy. At the saturated adsorption point, the adsorption amount of Bz was determined as nearly one Bz/**1** (Figure 4a), consistent with the above-mentioned single-component sorption experiment with Bz vapor in **1 $\alpha$**  (Figures S7 and S9). Gas chromatography determined the percentage of Bz adsorbed by **1 $\alpha$**  to be 97.5%, confirming the high selectivity of **1 $\alpha$**  over Bz (Figures 3b and S18), and the PXRD pattern of **1 $\alpha$**  totally changed upon uptake of the Bz/Cy mixture vapor but was consistent with the pattern of **1 $\alpha$**  after adsorption of Bz and the simulated pattern based on single-crystal data of Bz@**1** (Figure 4c). The above results indicated that **1 $\alpha$**  as a nonporous crystalline material selectively adsorbs

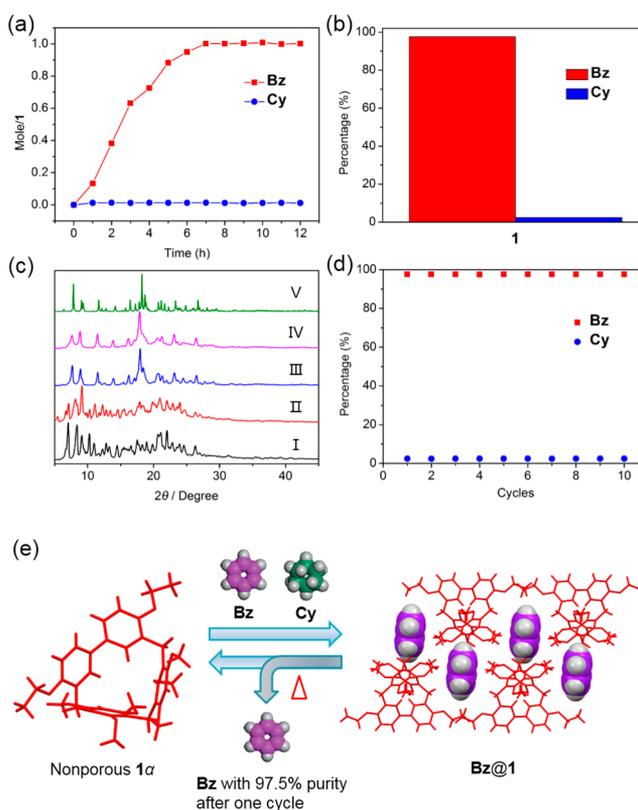


**Figure 3.** Single-crystal structure of Bz@1 at different views. (a–c) 1, red; C on Bz, purple; H on Bz, gray. (d) Illustration of C–H... $\pi$  and C–H...O interactions between 1 and Bz. H– $\pi$ -plane distances: A = 2.712 Å; B = 2.932 Å; C = 2.651 Å. H–O distance: D = 2.982 Å; C–H...O angle:  $\theta = 125.34^\circ$ . See Supporting Information for the structural details and CCDC number.

Bz from the Bz/Cy mixture, transforming the structure of 1 $\alpha$  into Bz@1 (Figure 4e).

In the real production, recycling capacity is a vital criterion for assessing an adsorbent. We proved that heating Bz@1 at 100 °C under vacuum removed adsorbed Bz and generated new crystals (Figures S19 and S20). In fact, the newly formed crystals were 1 $\alpha$ , as indicated by PXRD (Figure S21). Moreover, the newly formed 1 $\alpha$  was still able to selectively adsorb Bz from mixtures of Bz and Cy without losing performance after recycling 10 times (Figure 4d).

In summary, we have developed a new method to fully separate Bz from mixtures of Bz and Cy using nonporous adaptive crystals of a hybrid[3]arene (1 $\alpha$ ) for the first time. Furthermore, this work is the first example of hybridarene-based NACs used to separate hydrocarbons. We found 1 $\alpha$  separates Bz from a Bz/Cy equimolar mixture with a purity of 97.5%, indicating that 1 $\alpha$  is an excellent material for this separation. The selectivity mostly arose from the stability and variability of the newly formed crystal structure after adsorption of the preferred guest molecule. Moreover, the reversible transformations between the nonporous guest-free



**Figure 4.** (a) Time-dependent solid–vapor sorption plot of 1 $\alpha$  for Bz/Cy equimolar mixture vapor. (b) Relative uptakes of Bz and Cy adsorbed by 1 $\alpha$  over 12 h as measured by gas chromatography. (c) PXRD patterns of 1: (I) original 1 $\alpha$ ; (II) after adsorption of Cy vapor; (III) after adsorption of the Bz/Cy mixture vapor; (IV) after adsorption of Bz vapor; (V) simulated from single-crystal structure of Bz@1. (d) Relative uptakes of Bz and Cy by 1 $\alpha$  after 10 recycles. (e) Schematic representation of the transformation from 1 $\alpha$  to Bz@1 upon uptake of the Bz/Cy mixture vapor and the release of Bz by heating.

structure and the guest-containing structure made 1 highly recyclable. In view of the simple synthesis, high separation efficiency, and outstanding recycling performance of crystalline 1, this material possesses enormous potential for applications in the chemical industry. Future investigations will concentrate on producing various adaptive crystals of hybridarenes to realize more demanding adsorptive separation processes, such as gases, configurational isomers, isotopes, and chiral compounds.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.9b13548>.

Experimental details, NMR spectra, crystallography, and other materials (PDF)

X-ray crystallographic data for Bz@1 (CIF)

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## Notes

The authors declare no competing financial interest.

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