

Styrene Purification by Guest-Induced Restructuring of Pillar[6]arene

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Supporting Information

ABSTRACT: The separation of styrene (St) and ethylbenzene (EB) mixtures is important in the chemical industry. Here, we explore the St and EB adsorption selectivity of two pillar-shaped macrocyclic pillar[*n*]arenes (EtP5 and EtP6; *n* = 5 and 6). Both crystalline and amorphous EtP6 can capture St from a St-EB mixture with remarkably high selectivity. We show that EtP6 can be used to separate St from a 50:50 v/v St:EB mixture, yielding in a single adsorption cycle St with a purity of >99%. Single-crystal structures, powder X-ray diffraction patterns, and molecular simulations all suggest that this selectivity is due to a guest-induced structural change in EtP6 rather than a simple cavity/pore size effect. This restructuring means that the material “self-heals” upon each recrystallization, and St separation can be carried out over multiple cycles with no loss of performance.

Styrene (St) is an important aromatic feedstock in the chemical industry.¹ More than 80% of St production is used for polymerization or copolymerization to produce thermoplastics, synthetic rubbers, and resins. St is mainly produced by dehydrogenation of ethylbenzene (EB):² after dehydrogenation, the product stream still contains a large fraction (20–40%) of unreacted EB that must be removed.³ Separation by conventional distillation on an industrial scale is not practical because of the small difference in boiling point (9 K) between St (bp 418.3 K) and EB (bp 409.3 K). Currently, the preferred technology is extractive distillation and vacuum distillation, performed in the presence of polymerization inhibitors like phenylene-diamines or dinitrophenols.⁵ However, this is energetically intensive and most of the energy used in the production of St can be accounted for by the separation process. Also, small amounts of impurities with similar boiling points such as toluene (bp 393 K) and *o*-xylene (bp 418 K) must also be removed from the St-EB product stream, further complicating the procedure.^{3,4}

An alternative and potentially more energy-efficient separation strategy is to exploit the molecular, chemical, and geometrical differences of St and EB in an adsorptive separation, for example by using nanoporous materials such as metal–organic frameworks (MOFs) or zeolites.^{5–10} Adsorptive technologies do not require elevated temperatures, and hence the problem of side reactions can be circumvented, providing that the adsorbent itself is not reactive. However, the molecular sizes of St and EB are very similar (Figure 1a), making it difficult to find a suitable

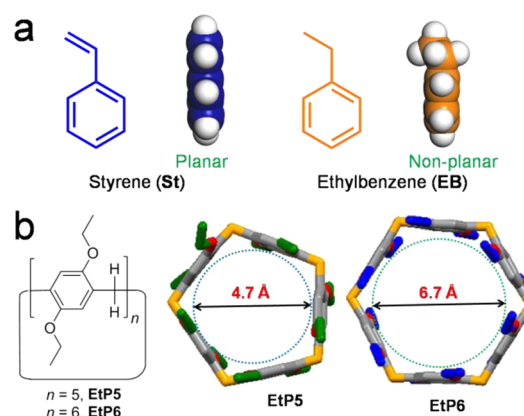


Figure 1. Chemical structures: (a) St and EB; (b) EtP5 and EtP6. The internal cavity diameters of EtP5 and EtP6 are based on the inscribed circle of the regular pentagon and hexagon, respectively.

porous material for their separation. In principle, crystallization-based separations can also be energy efficient. Unlike adsorptive separation, which uses materials with pre-existing pores, the “pores” in crystallization separation are created during assembly of the crystalline inclusion compound. These “pores” are generally only stable when occupied by guest molecules.¹¹ To our knowledge, no such separation method has been reported for styrene purification.

Pillar[*n*]arenes (*n* = 5–15) were first reported in 2008 as a novel class of supramolecular host.^{12–22} The host–guest properties of pillar[*n*]arenes have been investigated intensively and they have been applied in the fabrication of various supramolecular systems, such as interlocked structures, molecular machines, supramolecular polymers, and supramolecular amphiphiles.^{12–20} There are only a few occasions where pillar[*n*]arenes have been used as solid materials. For example, Yang et al. reported a pillar[5]arene-based supramolecular organic framework which has selective adsorption of CO₂ over N₂ at room temperature.²¹ Ogoshi et al. reported that a pillar[5]arene functionalized with ethyl groups could encapsulate *n*-alkanes in its cavity in the solid state.²²

Here, we investigate two pillararenes with different cavity sizes, perethylated pillar[5]arene (EtP5) and pillar[6]arene (EtP6) (Figure 1b), as adsorptive separation materials to separate St and EB. We show that both crystalline and amorphous EtP6 can

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selectively capture **St** from a mixture of **St** and **EB**. The adsorbed **St** molecules are located in the extrinsic pores between distorted **EtP6** molecules in a crystal structure that transforms to accommodate the **St** guest. The separation process for **EtP6** is a solid-state recrystallization separation, rather than an adsorptive separation. This process is quite different from separations that use porous adsorptive materials such as MOFs or zeolites, where intrinsic pore size and shape plays the determining role.

EtP5 and **EtP6** were synthesized by a previously reported method.¹⁹ Single crystals of **EtP5** and **EtP6** loaded with **St** and **EB** were obtained by slow evaporation of a **St** or **EB** solution of the pillararene, respectively. Despite numerous attempts, no diffractable single crystals could be grown of **St**-loaded **EtP5**. By contrast, **EB** forms a 1:1 host–guest complex with **EtP5** (**EB@EtP5**; **Figure 2a**, left). In **EB@EtP5**, an **EB** molecule is threaded

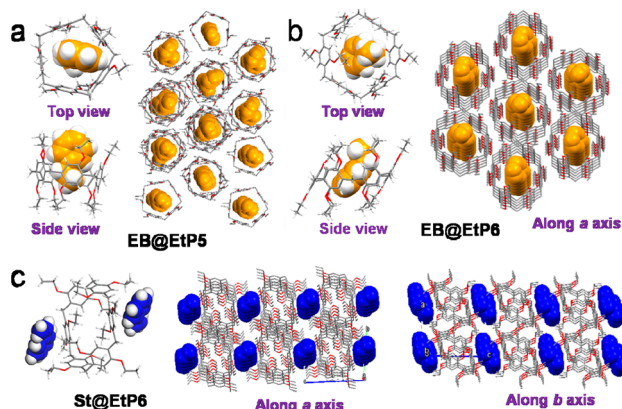


Figure 2. Single-crystal structures: (a) **EB@EtP5**; (b) **EB@EtP6**; and (c) **St@EtP6**. **St** is accommodated in 2D extrinsic channels between the pillararenes in **St@EtP6**.

into the cavity of **EtP5** with its ethyl group in the cavity center. This gives rise to $\text{CH}\cdots\pi$ interactions between the ethyl group on **EB** and the benzene rings on **EtP5**. The pentagonal structure of **EtP5** forms infinite 1D channels with **EB** in the channels (**Figure 2a**, right). In the analogous solvated crystal structure of **EtP6** (**EB@EtP6**), an **EB** molecule is located in the center of the cavity. This is stabilized by π – π stacking between **EB** and benzene rings on **EtP6**, also forming a 1:1 host–guest complex (**Figure 2b**, left). The hexagonal pillar structure of **EtP6** contributes to the formation of infinite intrinsic diagonal 1D channels with **EB** in the channels (**Figure 2b**, right). The solvated crystal structure of **EtP6** with **St** (**St@EtP6**) is markedly different. Two opposite repeating units of **EtP6** are turned perpendicular to their adjacent units, giving **EtP6** a more deformed hexagonal structure with a cavity that is too small to accommodate a **St** guest molecule (**Figure 2c**, left). However, the **EtP6** molecule does form infinite extrinsic 2D channels between the macrocycles along the *a* and *b* axes, with **St** molecules accommodated in these channels (**Figure 2c**, middle and right).

From these three crystal structures alone, it might be expected that **EtP6** has potential to selectively capture **EB** from a **St**–**EB** mixture due to its good fit in the **EtP6** intrinsic cavity. Solid–vapor adsorption experiments were performed to test this. Desolvated crystalline **EtP5** (**EtP5 α**) and **EtP6** (**EtP6 α**) were first prepared as adsorptive materials (for details, see the **Supporting Information**). Neither **EtP5 α** nor **EtP6 α** showed significantly different adsorption rates for **St** or **EB** vapor

(**Figures S7 and S9**). For **EtP5 α** , **EB** was adsorbed slightly faster than **St** whereas **EtP6 α** adsorbed both **St** and **EB** at similar rates. The major difference is the amount of **St** and **EB** adsorbed by **EtP6 α** , which is much higher than **EtP5 α** (**Figure S7**). To monitor the adsorption of neat **St** and neat **EB** by **EtP5 α** and **EtP6 α** , we carried out *in situ* PXRD studies. The PXRD patterns of **EtP5 α** did not change after adsorption of **St** or **EB**, indicating that the structure of **EtP5 α** did not change after exposure to **St** or **EB** (**Figure S8**). We concluded that **EB** or **St** was not, in fact, adsorbed in the bulk by **EtP5 α** . Instead, we ascribe the small, substoichiometric uptake of **St** (and **EB**) by **EtP5 α** to surface adsorption on the crystals. By contrast, the PXRD patterns of **EtP6 α** after adsorption of **St** or **EB** were different from **EtP6 α** and in good agreement with the simulated PXRD patterns for **St@EtP6** and **EB@EtP6**, respectively (**Figure S9b**). Hence, the adsorption of **St** or **EB** by **EtP6 α** triggers a crystal transformation from **EtP6 α** to **St@EtP6** or **EB@EtP6**, respectively (**Figure S9c**). **EtP6** is thus a more promising material than crystalline **EtP5** for the capture of **St** or **EB**.

To investigate whether **EtP6 α** could discriminate between a mixture of **EB** and **St**, we carried out time-dependent **EtP6 α** solid–vapor sorption experiments for a **St**–**EB** mixture (the **St**–**EB** mixture used is always 50:50 v/v). The uptake rates of **St** and **EB** in **EtP6 α** were essentially the same over the first hour (**Figure 3a**). Surprisingly, however, the uptake of **St** increased

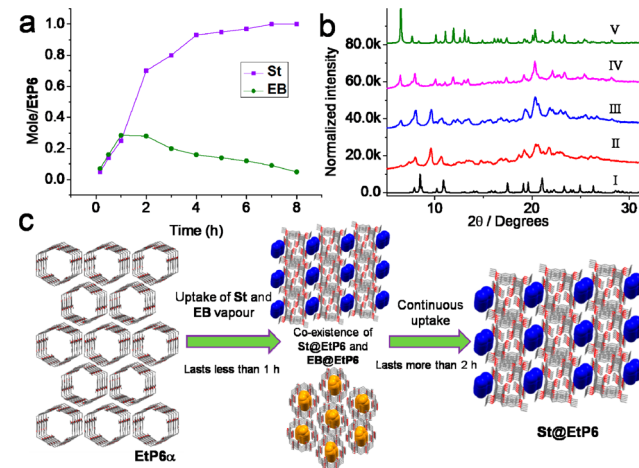


Figure 3. (a) Time-dependent **EtP6 α** solid–vapor sorption plot for **St**–**EB** mixture vapor. (b) Time-dependent PXRD patterns of **EtP6 α** : (I) simulated from single-crystal structure of **EB@EtP6**; after adsorption of **St**–**EB** mixture vapor for (II) 1 h, (III) 2 h, and (IV) 8 h; (V) simulated PXRD pattern from single-crystal structure of **St@EtP6**. (c) Representation of **EtP6 α** structural changes upon uptake of **St**–**EB** mixture vapor.

dramatically after the first hour and quickly increased to approximately 1 mol/**EtP6** after 4 h. The uptake of **EB** slowly decreased after the first hour, presumably because it was being displaced by **St** molecules and forced out of the intrinsic cavity as the structural transformation occurred. Gas chromatography was used to deduce the ratio of **St** and **EB** adsorbed by **EtP6 α** over the course of the experiment (**Figures S10 and S11**). This showed that **EtP6 α** could selectively capture **St** from a **St**–**EB** mixture, contrary to our initial hypothesis that **EB** might be selectively adsorbed. A time-dependent PXRD experiment was performed to monitor the transformation of **EtP6 α** after exposure to a **St**–**EB** mixture (**Figure 3b**). Comparison of the PXRD pattern recorded after adsorption of the **St**–**EB** mixture

vapor for 1 h with the simulated profiles of St@EtP6 and EB@EtP6 suggests the coexistence of St@EtP6 and EB@EtP6 phases after the initial exposure period (Figure S12). With increasing adsorption time, the PXRD pattern becomes more like St@EtP6 until it becomes fully consistent with the St@EtP6 structure. A putative mechanism, consistent with these observations is as follows: initially, the uptake rates of both St or EB in $\text{EtP6}\alpha$ are similar, and both St and EB can occupy empty $\text{EtP6}\alpha$ crystals, transforming them into two new polymorphs, St@EtP6 and EB@EtP6 . However, St@EtP6 is more stable than EB@EtP6 , and over time, St molecules diffuse into EB@EtP6 , displacing EB molecules and transforming EB@EtP6 into St@EtP6 .

We then carried out additional time-dependent solid–vapor sorption experiments using EB -loaded EB@EtP6 and St -loaded St@EtP6 to further investigate this guest-induced structural transformation. The uptake of St increased rapidly within 1 h when a St-EB vapor mixture was diffused into preloaded EB@EtP6 (Figure 4a). A saturation point was reached after

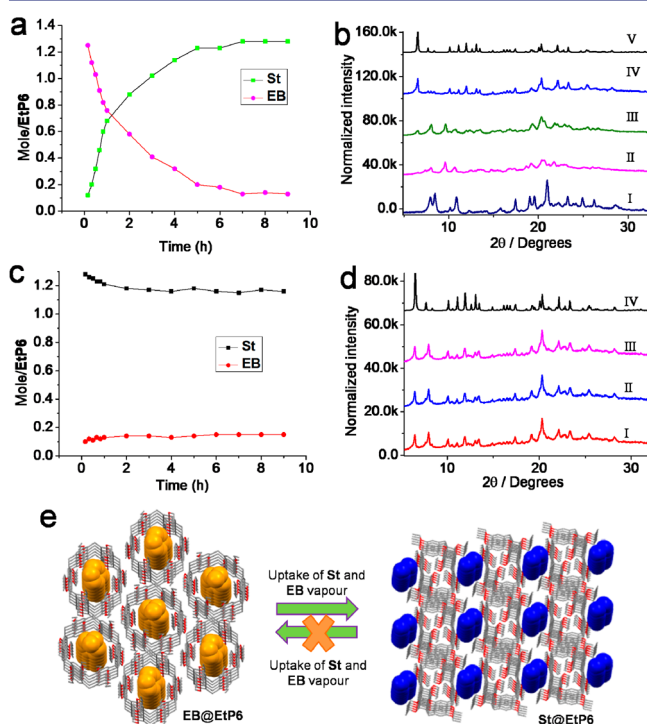


Figure 4. (a) Time-dependent $\text{EB@EtP6}\alpha$ solid–vapor sorption plot for St-EB mixture vapor. (b) Time-dependent PXRD patterns of EB@EtP6 : (I) original EB@EtP6 ; after adsorption of St-EB mixture vapor for (II) 1 h, (III) 2 h and (IV) 8 h; (V) simulated from single-crystal structure of St@EtP6 . (c) Time-dependent $\text{St@EtP6}\alpha$ solid–vapor sorption plot for St-EB mixture vapor. (d) Time-dependent PXRD patterns of St@EtP6 : (I) original St@EtP6 ; after adsorption of St-EB mixture vapor for (II) 1 h and (III) 8 h; (IV) simulated from single-crystal structure of St@EtP6 . (e) Structural representation of the irreversible transformation between St@EtP6 and EB@EtP6 upon uptake of St-EB mixture vapor.

about 7 h. EB , which was originally located in the 1D channels of EB@EtP6 , was displaced by St and its loading decreased as the St content increased. Time-dependent PXRD patterns (Figure 4b) indicate the guest-induced crystal-to-crystal transformation from EB@EtP6 to St@EtP6 over time. Hence, even when EB molecules were fully preloaded into crystals of EtP6 , St molecules in the St-EB mixture can penetrate these crystals and replace EB . By contrast, when fully solvated St@EtP6 is

exposed to the mixture of St-EB vapor, these crystals maintain a high loading of St and the EB uptake is negligible (Figure 4c). As expected, the PXRD pattern did not change at all, indicating that EB molecules in the St-EB mixture cannot replace St molecules in St@EtP6 (Figure 4d,e). This suggests that the St@EtP6 phase is more thermodynamically stable than the EB@EtP6 phase.

To rationalize this, we performed electronic density functional theory calculations to understand the structural stability of three EtP6 structures loaded with styrene molecules, i.e., (1) the experimental St@EtP6 phase; (2) the experimental EB@EtP6 phase with EB replaced by St , and; (3) the experimental $\text{EtP6}\alpha$ phase with St artificially inserted (the molar ratio of St and EtP6 = 1:1; St molecules were placed at the center of each EtP6). Table S4 summarizes the lattice energies determined for these three styrene-loaded structures. The experimentally observed St@EtP6 structure has the lowest lattice energy (-529 kJ/mol) among the three polymorphs, explaining its preferred formation.

To show that EtP6 has practical potential for styrene purification, we developed a procedure to obtain St with high purity from a St-EB mixture using crystalline EtP6 as the adsorbent. After adsorption of a St-EB vapor mixture, crystalline EtP6 was heated at 40 °C for 30 min to remove any unbound St or EB molecules adsorbed on the crystal surface. St could then be released from the selectively formed St@EtP6 phase with a purity of over 99% (Figure 5b).

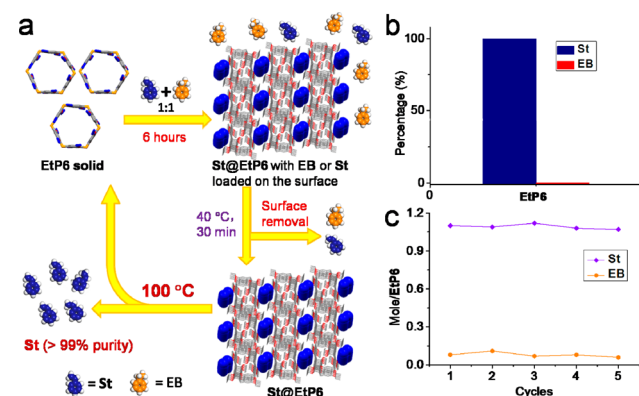


Figure 5. (a) Schematic representation of the general method to obtain highly pure St from a St-EB mixture using EtP6 as the adsorbent and the recycling of EtP6 . (b) Relative amount of St and EB in the resultant vapor measured by gas chromatography. (c) Maximum uptake of St and EB in EtP6 for 6 h after the same material is recycled five times.

One bane of adsorbent technology is decreased performance over time, because of either instability of the porous framework or fouling. To be practically useful, an adsorbent must perform well over multiple cycles without any degradation. Thus, an important question was whether the resultant desolvated EtP6 crystals can still selectively capture St from a St-EB mixture in a second cycle, after St is completely removed from the St@EtP6 crystals. Indeed, the desolvated St@EtP6 was shown by PXRD experiments to be a new polymorph, $\text{EtP6}\beta$ (Figure S17). Nonetheless, time-dependent solid–vapor experiments using the same St-EB vapor mixture showed that $\text{EtP6}\beta$ has adsorption properties for St and EB that are just like $\text{EtP6}\alpha$, indicating that $\text{EtP6}\beta$ can also selectively capture St from a St-EB mixture (Figure S20). PXRD experiments suggest the same selectivity mechanism as $\text{EtP6}\alpha$ and EB@EtP6 (Figure S21). Since the selectivity seems to be unaffected by this polymorphism in EtP6 , we further investigated whether amorphous EtP6 might also

have the same performance. Adsorption and PXRD experiments showed that amorphous EtP6 could also selectively adsorb St (Figures S24 and S25). As such, it is not necessary to use crystalline EtP6 for styrene purification and EtP6 can be recycled multiple times without losing its styrene selectivity or adsorption capacity (Figure 5c). Effectively, this crystallization route is a “self-healing” system: the separation works irrespective of the starting EtP6 structure. This is different from processes involving extended porous frameworks where loss of porosity or phase changes are often irreversible and catastrophic.

In summary, we have investigated the adsorptive properties of two easily obtained pillar[*n*]arenes, EtP5 and EtP6, toward St and EB. EtP6 was found to be a much better adsorbent for both St and EB, and either crystalline or amorphous EtP6 can selectively capture St from a St-EB mixture. This selectivity arises from the guest-induced selective structural change of EtP6 rather than the suitable cavity size. Compared with other small molecule organic separation materials, such as intrinsically porous cage compounds,²³ the separation process for EtP6 is closer to a crystallization separation, rather than an adsorptive separation. While the separation of St and EB has been achieved in porous extended frameworks, such as MOFs, this new molecular approach offers potential advantages. For example, EtP6 is soluble, is easy to synthesize, and has better chemical stability than many crystalline MOFs and COFs. While the overall uptake capacity in EtP6 is relatively low compared with porous extended frameworks, and the uptake kinetics are relatively slow, St can be separated with high purity in just one cycle, which is highly desirable. Future work will attempt to increase the uptake capacity and adsorption kinetics without losing the remarkable selectivity, for example by cocrystallization of two or three different pillar[*n*]arenes. Other hydrocarbon separations, such as the separation of xylene isomers, are also under investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13300.

Experimental details, crystallography, and other materials, including Figures S1–S25 and Tables S1–S4 (PDF)
X-ray crystallographic data for 2(EtP5)·4(THF), EB@EtP5, EtP6·3(acetone), EB@EtP6, and St@EtP6 (CIF)

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Notes

The authors declare no competing financial interest.

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