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Abstract: Haloalkanes are important chemicals in synthetic chemistry and petrochemical industry, but the separation of their isomers is a big hurdle. Herein, we report a facile energy-efficient adsorptive separation strategy using a new class of nonporous adaptive crystals based on leaning pillar[6]arene. Desolvated perethylated leaning pillar[6]arene crystals (EtLP6) with interesting nonporous character show a preference for 1-bromoalkane isomers over 2-bromoalkane isomers. EtLP6 is capable of separating 1-bromopropane, 1-bromobutane, and 1-bromopentane from the corresponding 1:1 (v/v) mixtures of 1/2-positional isomers with purities from 89.6 % to 96.3 % in only one adsorption cycle. The selectivity is endowed by the different host–guest binding modes and different stabilities of EtLP6 crystalloids loaded with 1- and 2-positional isomers. Significantly, the guest–adsorbed assemblies are highly stable at room temperature and EtLP6 can be reused many times without any decrease in performance.

Haloalkanes are high-value chemical feedstocks in synthetic chemistry and petrochemical industry, and their isomers are usually produced by direct halogenation of alkanes or alkenes and obtained as a mixture.\(^1\) Thus, the separation of haloalkane isomers is necessary and desirable to realize satisfactory broad applications. However, owing to their identical molecular weights, similar chemical structures, and close boiling points, it is unrealistic to employ traditional and energy-saving separation approaches such as distillation to separate haloalkane isomers with high purity.\(^2\) Although organic compounds with similar properties can be separated by commonly used azotropic distillation or extractive distillation in chemical industry, the high operation costs and environmental unfriendliness make the exploitation of economical and energy-efficient separation strategies for haloalkane isomers still imperative and in urgent need.\(^3\) Owing to their low energy consumption and environmental friendliness, nonthermally-driven adsorptive separations by synthetic materials, such as metal-organic frameworks (MOFs),\(^3,4\) porous organic polymers (POPs),\(^5\) covalent-organic frameworks (COFs),\(^6\) and supramolecular organic frameworks (SOFs),\(^7,8\) have been receiving tremendous attention in the past two decades, showing great potentials to revolutionize traditional industrial separation technology. However, the molecular sizes of primary (1−) and secondary (2−) haloalkanes are very close, making it hard to find a synthetic material with custom-built pores for separation, thus very limited examples have been presented.\(^1\)

Nonporous adaptive crystals (NACs) based on pillararanes, pioneered by Huang, Ogoshi, Cooper, and co-workers,\(^9\) are a new class of molecular-level solid materials. Completely different from traditional robust porous materials,\(^10,11\) NACs are nonporous in the initial state, but its intrinsic or extrinsic porosity can be induced by preferable vaporized species, accompanied with guest-loading crystalline phase transitions. This feature offers NACs great potential in the adsorption and separation of liquid-state organic targets during the process of construction and decomposition of specific solid-state host–guest assemblies. So far, no other synthetic macrocycle except pillararanes has been used to construct NACs for applications, neither such materials have been utilized to separate bromoalkane isomers.\(^9,11\)

In this work, we describe the first fabrication of NACs based on nonporous perethylated leaning pillar[6]arene (referred to as EtLP6, Figure 1a), a representative example of the new version of macrocyclic arenes named “leaning pillar[6]arenes” (or leaning towerarene) with desymmetrized ring structure, good cavity adaptability, and enhanced binding properties recently discovered by us,\(^2\) to realize the successful separation of 1-bromoalkane and 2-bromoalkane isomers (Figure 1b). EtLP6 could not only separate 1-bromopropane (1-BPR) from 2-bromopropane (2-BPR) with 89.6 % purity, 1-bromobutane (1-BBU) from 2-bromobutane (2-BBU) with 93.8 % purity, and 1-bromopentane (1-BPE) from 2-bromopentane (2-BPE) with 96.3 % purity through simple solid-vapor phase adsorption, but also exhibit great potential in sorting 1-chloralkane and 2-chloralkane isomers. Meanwhile, we further proved that the selectivity is arising from the different solid-state host–guest binding modes and the relative stability between the 1- and 2-positional isomers-loaded EtLP6 crystals. Significantly, removal of the trapped guests could transform the absorbed EtLP6 crystals back to the original guest-free form, enduring EtLP6 with excellent recycling property and application potential. EtLP6 was synthesized\(^2\) and then fabricated as adsorbent materials by simple recrystallization and desolvation (see the Supporting Information, Figures S1,S2). As suggested by powder X-ray diffraction (PXRD) data, the obtained EtLP6...
powders were crystalline (Supporting Information, Figure S3), and the 77 K N$_2$ sorption test indicated the nonporous nature (BET surface area of 3.07 m$^2$ g$^{-1}$, Figure S4 in the Supporting Information) and dense packing in the crystal state of EtLP6. In spite of its nonporous feature, NMR data and thermogravimetric (TG) analyses confirmed the effective adsorption capability of EtLP6 toward 1-bromoalkane and 2-bromoalkane isomers. Based on the $^1$H NMR spectra (Supporting Information, Figures S5–S7), the uptake amount of 1-BPR, 1-BBU, and 1-BPE were calculated to be one molecule per EtLP6 (Supporting Information, Figures S5–S7), while the uptake of 2-BPR, 2-BBU, and 2-BPE were less than the former (Supporting Information, Figures S8–S10), all agreed well with the TG results (Supporting Information, Figures S11–S16). On the other hand, PXRD studies were carried out to investigate the crystalline phase changes upon guest uptake. The PXRD patterns of EtLP6 showed varying degrees of changes after adsorption of 1-BPR, 1-BBU, 1-BPE, 2-BPR, 2-BBU, and 2-BPE, revealing the formation of guest-loaded crystalline new structures (Figure 1c,d). Interestingly, the PXRD patterns of EtLP6 after uptake of 1-BPR, 1-BBU, and 1-BPE were much alike (Figure 1c), and in the meantime exhibited similar changes of packing modes after adsorption of 2-BPR, 2-BBU, and 2-BPE, respectively (Figure 1d), indicating that EtLP6 transformed to the same crystal structure upon adsorption of these 1-bromoalkanes or 2-bromoalkanes. Therefore, in sharp contrast to traditional porous materials, crystalline phase changes and guest binding-triggered intrinsic porosity of EtLP6 are unique characteristics of the new NACs.

To reveal the actual solid-state structures, single crystals of EtLP6 loaded with 1-bromoalkanes and 2-bromoalkanes were obtained as 1-BPR$\subset$EtLP6, 1-BBU$\subset$EtLP6, 1-BPE$\subset$EtLP6, and 2-BPR$\subset$EtLP6 (Figure 2, and Supporting Information Tables S1,S2). For the binding series of 1-bromoalkane (1-BPR$\subset$EtLP6, 1-BBU$\subset$EtLP6, and 1-BPE$\subset$EtLP6), the ring-forming monomers of EtLP6 are tilted and the ethyl groups occupy its cavity; each 1-bromoalkane (1-BPR, 1-BBU, and 1-BPE) molecule is located outside the cavity and sandwiched between two adjacent EtLP6 rings by the stabilization of multiple C$\equiv$H$\cdots$π interactions (Figure 2a–c, left). The PXRD patterns of EtLP6 after uptake of 1-BPR, 1-BBU, and 1-BPE matched well with the simulated patterns from the crystal structures of 1-BPR$\subset$EtLP6, 1-BBU$\subset$EtLP6, and 1-BPE$\subset$EtLP6, respectively (Figure 3d–f), further confirming the transition from guest-free to guest-loaded structures. It is worth noting that 1-BPR, 1-BBU, and 1-BPE are statistically disordered intracrystalline, and two identical chain motifs with a symmetric center (red point) could be refined simultaneously, so each has an occupancy of 0.5 (Figure 2a–c, right, and Scheme S1 in the Supporting Information).

In terms of 2-bromoalkane-loaded single crystal structures, 2-BBU and 2-BPE loaded crystal structures (2-BBU$\subset$EtLP6, 2-BPE$\subset$EtLP6) were not available by common crystal growth methods due to the molecular chirality of 2-BBU and 2-BPE. However, according to the similar PXRD patterns of 2-BPR$\subset$EtLP6, 2-BBU$\subset$EtLP6, and 2-BPE$\subset$EtLP6 as aforementioned (Figure 1d), the single

Figure 1. Chemical structures of a) perethylated leaning pillar[6]arene (EtLP6) and b) 1-bromopropane (1-BPR), 2-bromopropane (2-BPR), 1-bromobutane (1-BBU), 2-bromobutane (2-BBU), 1-bromopentane (1-BPE), and 2-bromopentane (2-BPE). c) Powder X-ray diffraction (PXRD) patterns of EtLP6 during 1-bromoalkane adsorption: (I) original EtLP6; after adsorption of (II) 1-BPR vapor, (III) 1-BBU vapor, and (IV) 1-BPE vapor. d) PXRD patterns of EtLP6 during 2-bromoalkane adsorption: (I) original EtLP6; after adsorption of (II) 2-BPR vapor, (III) 2-BBU vapor, and (IV) 2-BPE vapor.

Figure 2. Single crystal structures: a) 1-BPR$\subset$EtLP6. b) 1-BBU$\subset$EtLP6. c) 1-BPE$\subset$EtLP6. d) 2-BPR$\subset$EtLP6. 1-Bromoalkanes in 1-BPR$\subset$EtLP6, 1-BBU$\subset$EtLP6, and 1-BPE$\subset$EtLP6 crystals are statistically positional disordered (50:50, either set is independently occupied).
A crystal structure of 2-BPR·EtLP6 was obtained to represent and also used for the investigation of the solid-state host–guest interactions between the 2-bromoalkane molecules and EtLP6 (Figure 2d). To our surprise, in sharp contrast to the 1-bromoalkane-loaded structures, EtLP6 in 2-BPR·EtLP6 exhibited an interesting guest bulkiness-induced conformation change, showing a deformed hexagonal structure with a 2-BPR molecule included inside the cavity and stabilized by moderate C–H···π and C–H···O interactions (C–H···π distance: 2.824 Å, C–H···O distance: 2.871 Å, Figure 2d, left). In the meantime, the EtLP6 molecules also formed honeycomb-like infinite 1D channels along the (0, 1, 0) directions (Figure 2d, right). Based on the crystal structure analysis, we deduced that the 1-bromoalkane-loaded crystals could be more stable than their corresponding 2-bromoalkane-loaded ones. Thus, differential scanning calorimetry (DSC) measurements were performed to investigate the relative stability of 1-bromoalkane and 2-bromoalkane loaded EtLP6 crystals (Supporting Information, Figures S17–S23). For instance, the nearly 40°C difference of the guest released temperature between 1-BPR·EtLP6 (120°C) and 2-BPR·EtLP6 (80°C) (Supporting Information, Figures S18,S19), far beyond their normal boiling point difference (11°C; b.p. of 1-BPR: 71°C, b.p. of 2-BPR: 60°C), strongly supported the different stabilities of 1-BPR·EtLP6 and 2-BPR·EtLP6 as concluded from the single crystal analysis.

Considering the different binding modes, we envision that EtLP6 may process the ability to discriminate a 1-bromoalkane and 2-bromoalkane isomers mixture. A time-dependent solid-vapor sorption experiment of EtLP6 with three groups of 1-bromoalkane and 2-bromoalkane isomers was conducted (Supporting Information, Figures S24–S32). As expected, the uptake of 1-BPR, 1-BBU, and 1-BPE in EtLP6 was way larger than 2-BPR, 2-BBU, and 2-BPE, respectively, and the uptake rate of 1-bromoalkane was greater, which varied from 1 to 4 h to reach each saturated adsorption point (Figure 3a–c). In accordance with the crystal structures, the uptake amount of 1-BPR, 1-BBU, and 1-BPE in EtLP6 can be determined as nearly one Mole per EtLP6. Gas chromatography (GC) data also supported that EtLP6 has a high selectivity for 1-bromoalkane (89.6% for 1-BPR, 93.8% for 1-BBU, and 96.3% for 1-BPE, Figure 4a,b, and Figures S33–S35 in the Supporting Information), and the PXRD patterns of the guest-absorbed EtLP6 crystals are all in consistency with the simulated patterns of the 1-BPR·EtLP6, 1-BBU·EtLP6, and 1-BPE·EtLP6 (Figure 3d–f), displaying a structural transition from the guest-free EtLP6 crystals to the 1-bromoalkane-loaded crystals upon selective capture. It is noteworthy that the selectivity toward 1-bromoalkane and 2-bromoalkane isomers can be enhanced with the increase of carbon atoms of 1-bromoalkane, which implies that more linear carbon chain in the preferable guests will be endowed with much stronger C–H···π interactions with EtLP6 and the adsorption selectivity in the specific sandwich-like host–guest binding. Nonporous EtLP6 crystals can distinguish 1-chlorobutane (1-CBU) from 2-chlorobutane (2-CBU) in the same pattern (Supporting Information, Figures S36–S50). Single crystal structure and PXRD pattern of 1-CBU-loaded EtLP6 (1-CBU·EtLP6) showed the same solid-state host–guest binding mode with 2-BBU·EtLP6 (Supporting Information, Figures S40,S41), presenting a similar purification power.

Figure 3. Time-dependent EtLP6 solid-vapor sorption plot for (a) 1-BPR/2-BPR mixture vapor, (b) 1-BBU/2-BBU mixture vapor, and (c) 1-BPE/2-BPE mixture vapor at room temperature. d) PXRD patterns of EtLP6: (I) original EtLP6, after adsorption of (II) 2-BPR vapor, (III) 1-BPR vapor, and (IV) 1-BPR/2-BPR mixture vapor; (V) simulated PXRD pattern from single-crystal structure of 1-BPR·EtLP6. e) PXRD patterns of EtLP6: (I) original EtLP6, after adsorption of (II) 2-BBU vapor, (III) 1-BBU vapor, and (IV) 1-BBU/2-BBU mixture vapor. (V) simulated PXRD pattern from single-crystal structure of 1-BBU·EtLP6. f) PXRD patterns of EtLP6: (I) original EtLP6, after adsorption of (II) 2-BPE vapor, (III) 1-BPE vapor, and (IV) 1-BPE/2-BPE mixture vapor. (V) simulated PXRD pattern from single-crystal structure of 1-BPE·EtLP6.
kane isomers along with a phase change from amorphous to guest-loaded structures (Supporting Information, Figures S73–S76), totally different from the adsorption and purification process launched by many traditional crystalline porous frameworks\cite{7,9a} where phase change or porous degradation always means losing or decreasing its performance. Overall, \textcolor{red}{EtLP6} proved to be powerful and practical for separation of 1-bromoalkane and 2-bromoalkane isomers owing to its simple operating, remarkable efficiency, and recyclability.

In conclusion, we investigated the separation of 1-bromoalkanes and 2-bromoalkanes isomers using new NACs based on a unique leaning towerarene. \textcolor{red}{EtLP6} could selectively uptake 1-bromoalkane isomers over their 2-positional isomers by simple solid-vapor adsorption, no matter if in its crystalline or amorphous modes. This selectivity derived from the different solid-state host–guest binding modes and the relative stability between the 1-bromoalkane and 2-bromoalkane-loaded crystal structures. In consideration of the inexpensive raw materials and facile synthesis, leaning pillar[6]arene-based crystalline separation materials, such as nonporous \textcolor{red}{EtLP6} in this work, offers plenty of merits. We strongly believe that the investigation of adsorption and separation applications will be one of the important development directions of synthetic macrocycles and molecular crystals. Other demanding isomer separations by leaning pillar[6]arenes and other synthetic macrocyclic arenes are still ongoing in our laboratory.

\textbf{Acknowledgements}

We gratefully acknowledge the National Natural Science Foundation of China (21871108), Jilin Province-University Cooperative Construction Project-Special Funds for New Materials (SXSJSF2017-3), and Jilin University Talents Cultivation Program for financial support.

\textbf{Conflict of interest}

The authors declare no conflict of interest.

\textbf{Keywords:} host–guest systems · isomers separation · leaning pillar[6]arene · nonporous adaptive crystals · supramolecular chemistry

\textbf{How to cite:} Angew. Chem. Int. Ed. 2020, 59, 2251–2255

\textcolor{red}{Angew. Chem. 2020, 132, 2271–2275}

\begin{thebibliography}{99}
\end{thebibliography}


[13] CCDC 1937374, 1937375, 1937376, 1937377, and 1937378 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Manuscript received: September 18, 2019
Revised manuscript received: November 24, 2019
Accepted manuscript online: November 25, 2019
Version of record online: December 27, 2019