High-Performance n-Hexane Purification by Nonporous Adaptive Crystals of Leaning Pillar[6]arene

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The production of high-purity n-hexane under mild conditions is of great significance in both the petrochemical industry and synthetic chemistry. Here, we report an easy-to-operate and energy-efficient n-hexane purification strategy using nonporous adaptive crystals of perethylated leaning pillar[6]arene (EtLP6). Adaptive EtLP6 crystals preferentially absorb n-hexane over other branched or cyclic C6 alkanes with similar boiling points. This selectivity arises from the different thermodynamic stabilities and variabilities of EtLP6 crystalloids loaded with n-hexane and other C6 alkanes. Moreover, the reversible transformations between the nonporous guest-free and n-hexane-containing structures make the EtLP6 crystals highly recyclable.

Keywords: supramolecular chemistry, nonporous adaptive crystals, leaning pillar[6]arene, molecular separation, host–guest systems

Introduction

Alkanes are very important feedstocks in the chemical and petrochemical industries.1 n-Hexane (nHex), as a broad-spectrum n-alkane, is generally produced from the distillation of raffinate oil (composed of C6 alkane mixtures) in the chemical industry and is always obtained with a small percentage of methylcyclopentane (Mcp) and other C6 impurities.2–7 which must be further purified to obtain nHex with high purity. However, the remarkably close boiling points of nHex and Mcp (boiling points, n-Hex: 68.7 °C, Mcp: 71.8 °C) make them practically impossible to separate by distillation. Besides, other C6 impurities with relatively approximate boiling points, such as cyclohexane (80.7 °C), 2-methylpentane (60.3 °C), 3-methylpentane (63.3 °C), and 2,3-dimethylbutane (58.7 °C) (Figure 1a), should also be taken into consideration, which further complicate the procedures. Specifically for n-Hex and Mcp, the present major technologies are azeotropic distillation and extractive distillation,7 and the search for more simple and energy-efficient separation strategies by scientists still continues.8–13 Nonthermally-driven nHex adsorptive separation by synthetic porous adsorbents, such as metal–organic frameworks (MOFs),14–21 zeolites,22–24 and carbon molecular sieves,25 is routinely described as a potential sorting
method. However, due to the lack of highly polar groups, alkanes always possess low binding affinity toward these materials.\textsuperscript{26,27} Meanwhile, MOFs are constructed on the basis of reversible chemistry attributed to the existence of bridging coordination entities, facing potential problems of instability upon cycling. Thus, the separation of alkanes using porous packing materials is time-consuming and inefficient, and the development of new adsorbents is imperative and desirable.

Very recently, Huang’s group, Li’s group, Sue’s group, and our group have demonstrated that nonporous adaptive crystals (NACs) of pillararenes,\textsuperscript{28-37} biphenarenes,\textsuperscript{38} geminiarene,\textsuperscript{39} tiarene,\textsuperscript{40} hybridarene,\textsuperscript{41} and leaning pillararenes (leaning tower[6]arenes)\textsuperscript{42} display remarkable potential in hydrocarbon separation. Totally different from traditional porous crystalline materials,\textsuperscript{43-46} NACs seem nonporous in the initial state, but its intrinsic and/or extrinsic porosity can be triggered and induced by specific vaporized guests via solid-state host–guest interactions including C–H⋯π interactions, aromatic π⋯π stacking, and/or charge-transfer interactions, offering great possibilities for highly selective guest uptake by extrusion with incompatible species. Besides, NACs possess many advantages including excellent thermal and chemical stabilities, organic solvent-free, and good moisture resistance.

Here, for the first time, we utilize NACs of leaning pillar[6]arenes to purify nHex (Figure 1b). We found that nonporous perethylated leaning pillar[6]arene (EtLP6) crystals could separate nHex from an equimolar mixture of nHex–Mcp with a purity of about 97%, through methods of both lossless solid–vapor phase adsorption and high-speed solid–liquid phase adsorption. Meanwhile, we have further demonstrated that the selectivity of EtLP6 NACs toward nHex remains in relatively complicated C6 alkanes/cyclanes mixed systems. Crystal structural analyses in conjunction with powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) experiments reveal that the selectivity comes from the different solid-state host–guest binding modes/affinities and thermodynamic stabilities between the nHex-loaded and other C6-loaded EtLP6 crystals. Moreover, removal of the trapped nHex from nHex-loaded EtLP6 crystals leads to the reconstructed, original guest-free crystalline phase, making the nonporous EtLP6 crystals highly recyclable without losing selectivity or capacity performance.

**Experimental Methods**

The alkane/cyclane mixtures used in the present study are always equivoluminal unless otherwise noted. For each solid–vapor adsorption experiment, an open 0.5 mL vial containing 3 mg of activated EtLP6 crystals was placed in a sealed 2 mL vial containing 0.03 mL of an nHex–Mcp mixture solution. For each solid–liquid adsorption experiment, 5 mg of activated EtLP6 crystals were placed in a sealed 2 mL vial containing 0.05 mL of C6 alkanes/cyclanes (respective or hybrid). Guest uptake in EtLP6 crystals was measured hour by hour by completely

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**Figure 1 | Chemical structures and representations: (a) n-hexane (nHex), methylcyclopentane (Mcp), 2-methylpentane (2Mep), 3-methylpentane (3Mep), 2,3-dimethylbutane (23Dmb), and cyclohexane (Ch); (b) perethylated leaning pillar [6]arene (EtLP6).**

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dissolving the crystals and measuring the ratio of nHex and Mcp to EtLP6 by $^1$H NMR, respectively. The relative uptakes of C6 alkanes/cyclanes in EtLP6 crystals were also measured by dissolving the crystals in DMF to release the adsorbed species using gas chromatography. More experimental details and characterization are available in the Supporting Information.

Results and Discussion

Activated guest-free EtLP6 crystalloid powders as adsorptive separation materials (Supporting Information Figures S3–S5) and n-hex-containing EtLP6 crystal structures (nHex$\subset$EtLP6) were obtained according to previous reports, while no single crystal of Mcp-loaded...
EtLP6 was obtained due to the weak host–guest interactions between EtLP6 and Mcp. Interestingly, through the similar crystal growth method used for nHexEtLP6 (for details, see the Supporting Information), only a 1:4 host–guest assembly between EtLP6 and CHCl₃ was obtained (Supporting Information Table S1, Figures S1 and S2), which indicated that, in the crystalline state, nHex possesses the strongest binding affinity toward EtLP6, CHCl₃ is next, and Mcp is last. Mechanistically, in nHexEtLP6, all the phenylene units of EtLP6 are tilted and the alkyl groups occupy its own cavity, and, legitimately, each nHex molecule is located outside the cavity and sandwiched between two adjacent-substituted phenylene units, stabilized by multiple C–H⋯π interactions (Figure 2a, right). On the macroscale, the leaning tower conformation and sandwich-like solid-state binding mode of EtLP6 lead to the formation of extrinsic 1D channels along an axis, with nHex molecules stably housed within.

Based on these crystal structure analyses, we deduced that EtLP6 possesses the ability to discriminate nHex from the nHex/Mcp mixture. First, solid–vapor sorption experiments toward a single-component nHex or Mcp vapor were conducted (Supporting Information Figures S6–S15). Time-dependent solid–vapor sorption experiments showed that the uptake amount of nHex in EtLP6 steadily increased within a few hours and was calculated to be 0.88 mol nHex/mol EtLP6 after saturation (Supporting Information Figures S8 and S9). In contrast, little adsorption of Mcp was observed under identical conditions (Supporting Information Figure S10). The PXRD pattern of EtLP6 after adsorption of nHex vapor was different from the original activated form and matched well with the simulated pattern of nHexEtLP6 (Figure 2b–I, III, and V). On the contrary, no phase change was found after adsorption of Mcp vapor, further indicating the lack of effective Mcp loading during the adsorption process (Figure 2b–I and II). Meanwhile, TGA and DSC data show that the temperature of nHex released from the adsorbed EtLP6 crystalloids is ca. 110 °C (Supporting Information Figures S11 and S14), far beyond its normal pressure boiling point (68.7 °C), strongly proving the adsorption and storage capability of nonporous EtLP6 crystals toward nHex.

The aforementioned data suggest that EtLP6 is a promising crystalline material for the capture of nHex rather than Mcp. Thus, a time-dependent solid–vapor sorption experiment for a mixture of nHex–Mcp (v:v = 1:1) was carried out (Figures 2a–2e, Supporting Information Figures S16–S20). Similar to the single-component sorption experiments, the uptake of nHex by activated EtLP6 crystals increased over time and reached a saturation point over 15 h, while the adsorption of Mcp remained extremely low (Figure 2c). Gas chromatography (GC) experiments showed that the percentage of nHex adsorbed in EtLP6 was 97.1% (Figure 2d), further confirming its remarkably high selectivity toward nHex. The PXRD pattern of EtLP6 after adsorption of the nHex–Mcp mixture vapor is fully consistent with the simulated pattern from nHexEtLP6 (Figure 2b–IV and V), confirming its remarkably high selectivity toward nHex. The PXRD pattern of EtLP6 after adsorption of the nHex–Mcp mixture vapor is fully consistent with the simulated pattern from nHexEtLP6 (Figure 2b–IV and V).

**Figure 3** (a) Schematic representation of the solid–liquid uptake method for nHex purification. nHex-loaded host–guest assemblies were prepared by immersion of EtLP6 in bulk alkanes/cyclanes followed by filtration of the resulting crystals. (b) Time-dependent EtLP6 solid–liquid sorption plot for nHex/Mcp mixture. (c) Typical GC traces of the purities of nHex in EtLP6 after immersion in (I) Mix-b, (II) Mix-a, (III) equimolar nHex/Mcp, and (IV) nHex/Mcp (v/v = 12/1) mixtures.

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indicating the phase transition from the activated EtLP6 crystals to nHexEtLP6 upon selective vapor capture. Moreover, guest-free EtLP6 crystals could be easily reconstructed by heating the adsorbed crystals at 130 °C in vacuum for 12 h, and no obvious decrease in selectivity toward nHex was observed after reusing the same material for another four adsorption-desorption cycles (Figure 2e), implying preeminent recycling properties of EtLP6 crystals. In brief, completely different from conventional porous frameworks, crystalline phase change triggered by preferential guest molecules is a unique advantage of the selective adsorption of NACs of EtLP6.

Although nonporous EtLP6 crystals possess an outstanding adsorption selectivity toward nHex from the solid–vapor sorption experiments, the adsorption rate is moderate, which is far from its practical use. Thus, we further adopted additional solid–liquid sorption experiments to enhance its adsorption performance (Figure 3a and Supporting Information Figures S21–S27). As depicted in Figure 3b, the uptake amount of nHex in EtLP6 dramatically increased within the first hour and was calculated to be 0.93 mol nHex/mol EtLP6 after saturation (Supporting Information Figures S26 and S27). Similar to the solid–vapor sorption experiments, trace amounts of Mcp were adsorbed and observed during the whole adsorption process, and the purity of nHex absorbed in EtLP6 was determined to be 96.8% by GC (Figure 3c–III). Besides, the crystalline phase changes, uptake capacity, and the recycling properties of EtLP6 after selective adsorption of the nHex–Mcp mixture liquid are all consistent with previous solid–vapor sorption experiments (Supporting Information Figures S29–S33). Furthermore, the purity of nHex absorbed in EtLP6 could even reach 99.5% by mimicking a more actual ratio of nHex/Mcp (12:1, v:v) in the raffinate oil (Figure 3c–IV), suggesting the great potential of EtLP6 in nHex purification.

Considering the sorption abilities, there was interest to determine whether EtLP6 crystals still possess the capability in nHex purification in more complex alkane mixtures. Anti-interference experiments by introducing another four C6 alkanes/cyclanes with small differences in boiling points were taken into account, that is, 2-methylpentane (2Mep), 3-methylpentane (3Mep), 2,3-dimethylbutane (23Dmb), and cyclohexane (Ch) (Figure 1b). Two nHex-containing mixtures, one composed of nHex, Mcp, 3Mep, 2Mep, and 23Dmb (Mix-a for short, v:v:v:v:v = 1:1:1:1:1) and the other composed of nHex, Mcp, 3Mep, 2Mep, and Ch (Mix-b for short, v:v:v:v:v = 1:1:1:1:1), were used to determine the interference effects of other alkanes/cyclanes on the selectivity of EtLP6 toward nHex. GC experiments showed that the percentages of nHex absorbed in EtLP6 crystals were 93.3% (from Mix-a, Figure 3c–II, Supporting Information Figures S35) and 78.8% (from Mix-b, Figure 3c–I, Supporting Information Figures S36), respectively, and the DSC heating curves of the EtLP6 crystals after adsorption from the equimolar nHex–Mcp mixture, Mix-a, and Mix-b only showed the same endothermic peak related to the desorption of the trapped nHex molecules (Figure 4a). Moreover, PXRD patterns of EtLP6 after adsorption of Mix-a and Mix-b are all in good agreement with the simulated patterns of nHexEtLP6 (Figure 4b), which strongly confirm the excellent anti-interference capabilities of EtLP6 in the purification of nHex molecules.

Interestingly, upon immersing the activated EtLP6 crystals in the liquids of Mcp, 3Mep, 2Mep, 23Dmb, and Ch, respectively, only Ch molecules triggered an obvious guest-loading process (Supporting Information Figures S34–S38).
Figures S37). Thus, to better understand the selective mechanisms toward nHex, single crystals of EtLP6 loaded with Ch were obtained (Ch⊂EtLP6). Unexpectedly, in sharp contrast to the nHex-loaded structures as mentioned before, EtLP6 in Ch⊂EtLP6 exhibited an interesting guest-induced conformation change, where a hexagonal pillar structure with unsubstituted phenylene units moderate tilt was clearly presented (Figure 5a). As expected, Ch molecules existed in the cavity of EtLP6, but could not be precisely defined/refined due to the weak in-cavity host-guest interactions in the solid state. Also, according to the DSC heating curves, each group of activated EtLP6 crystals after being immersed in Mcp, 3Mep, 2Mep, and 23Dmb liquids possess the same phase transition peak (from 140 °C to 160 °C, Figure 5b) like being immersed in Ch, implying that they all experienced a similar crystal-to-crystal transformation from guest-loaded to original guest-free EtLP6 crystals, just like the structure of the Ch-loaded structure (Ch⊂EtLP6). However, only partial phase changes and less amounts of guest uptake were found in these branched-C6 liquids, different from the complete phase conversion and full guest uptake in Ch (Supporting Information Figures S37 and S38). Hence, we have reasons to believe that this selectivity toward nHex is attributed to the relative stability between the nHex and other C6-alkanes/cyclanes-loaded structures, that is, stronger and more regular C–H···π interactions between nHex and EtLP6 lead to the formation of nHex⊂EtLP6 with higher thermodynamic stability than other C6 species loaded forms, further resulting in intrinsic linear selectivity.

Conclusion

In conclusion, we investigated the purification of nHex using nonporous EtLP6 crystals. Activated EtLP6 crystals were first applied to separate nHex from a nHex/Mcp equimolar mixture with a high purity of about 97%, both through the approaches of lossless solid–vapor phase adsorption and high-speed solid–liquid phase adsorption. Furthermore, anti-interference experiments by introducing other branched/cyclic C6 alkanes confirmed that EtLP6 crystals can still retain their selectivity toward nHex in more complicated C6 conditions. The selectivity toward nHex is derived from different thermodynamic stabilities between the nHex and other C6 species-loaded EtLP6 crystal structures. Compared with conventional porous materials, NACs of EtLP6 as a new candidate for alkane sorting offer plenty of merits, such as low cost, scalable synthesis, good processability, thermal/chemical stability, and high recyclability. Our future works are expected to solve more challenging separation problems by using leaning pillararenes and/or their derivatives, such as the separation of cis-/trans-isomers and configurational isomers.

Supporting Information

Supporting Information is available.

Conflict of Interest

There is no conflict of interest to report.

Acknowledgments

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Figure 5 | (a) Single-crystal structure of Ch⊂EtLP6. Ch molecules were removed due to their high disorder during structure refinement. (b) DSC heating curves of EtLP6: (I) activated EtLP6; after immersion in (II) Mcp, (III) 2Mep, (IV) 3Mep, (V) 23Dmb, and (VI) Ch.
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