Synthetic Macrocycle-Based Nonporous Adaptive Crystals for Molecular Separation

Jia-Rui Wu and Ying-Wei Yang*

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Aromatics/Cyclic Aliphatics separation
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Haloalkanes separation
Cis-trans isomers separation
Heterocyclic isomers separation
Macroyclic NACs
The exploitation of new materials for adsorptive separation of industrially important hydrocarbons is of great importance in both scientific research and petrochemical industry. Nonporous adaptive crystals (NACs) as a robust class of synthetic materials have drawn much attention during the past five years for their superior performance in adsorption and separation. Pillararenes are the main family of macrocyclic arenes used for NACs construction, where the structure–function relationship has been intensively studied. In the past two years, some emerging types of synthetic macrocyclic arenes have been successfully brought into this research field, showing the gradual enrichment and diversification of NACs materials. This Minireview summarizes the recent advances of synthetic macrocycle-based NACs, which are categorized by various practical applications in molecular separation. Besides, NACs-based vapochromic supramolecular systems are also discussed. Finally, future perspectives and challenges of NACs are given. We envisage that this Minireview will be a useful and timely reference for those who are interested in new molecular and supramolecular crystals for storage and separation applications.

1. Introduction

The past two decades have witnessed the boom and rapid development of crystalline organic materials based on supramolecular macrocycles. These crystalline organic materials can be constructed either by assembling the macrocycles by noncovalent interactions or through the covalent bonding of macrocycles with certain organic linkages. Interestingly, some macrocycle-based crystalline organic materials exhibit intrinsic and extrinsic porosity, i.e., multiporosity, resulting from the prefabricated cavities and inefficient molecular packing of certain macrocycles in the crystalline state. Besides the apparent porosity, an intriguing feature of macrocycle-based crystalline organic materials is that they may possess porosity “without pores”, mainly because the seemingly nonporous materials possess cavities and/or lattice voids available to guest species despite of non-atomic-scale channels in the crystal structures. Another specific feature for certain macrocycle-based crystalline organic materials is that they are nonporous but structurally adaptive to changes, that is, their crystalline structures could be transferred from high-density guest-free one to low-density guest-containing version upon exposure to specific guests, where typical examples are nonporous crystals or nonporous adaptive crystals (NACs) of macrocycles.

In comparison with multifarious macromolecular or molecular level porous materials, such as supramolecular organic frameworks, metal-organic frameworks, porous organic polymers, zeolites, hydrogen-bonded organic frameworks and porous organic cages, which usually possess large intrinsic surface area and well-defined pore structures/dimensions, macrocycle-based NACs seem nonporous in the initial state due to the densely molecular packing, but their porosity could be opened by suitable guest species via supramolecular interactions, thus forming corresponding solid-state host–guest assemblies along with guest-induced crystalline phase transformation. This unique property enables NACs to work at the supramolecular level and can generate custom-built voids to selectively accommodate guests/cargos. Besides, synthetic macrocycle-based NACs offer plenty of merits, such as easy preparation, low cost, high recyclability, chemical resistance, and thermal stability.

The pursuit of macrocycle-based nonporous crystals can be traced back to early 2000s. In 2002, Atwood et al. first described that guest species could transport through the lattice of the crystals of \(p\)-tert-butylcalix[4]arene along with the single crystal-to-single-crystal transformations, although the fact that there is no obvious channels/poreosity in its structure. During the past five years, NACs of pillararenes have attracted considerable interest as they display great potentials for practical applications, especially in the adsorption, separation, and storage of hydrocarbons. In 2015, Ogoshi et al. reported the first example of pillar[4]arene-based crystalline state vapor uptake. Then, the continuous research efforts by the Huang group and the Ogoshi group have clearly demonstrated that pillararenes-based NACs or molecular crystals can serve as excellent candidates for separation of hydrocarbon mixtures, including alkane isomers (isoctane/n-heptane), olefin isomers (CS linear positional isomers), C8-aromatics (styrene/ethylbenzene and xylene isomers) aromatics/cyclic aliphatics mixture (toluene/methylcyclohexane) and halohydrocarbons isomers (1,2-chlorobutane isomers and dihalobenzene isomers). Meanwhile, NACs of pillararenes can also serve as effective adsorbents for iodine and dioxane. Major findings can be summarized into four categories: (a) NACs of pillararenes can discriminate molecules in their gas sorption isotherms by different gate-opening behaviors, especially those with slight differences in size, shape, and boiling point; (b) the gate-opening process is always accompanied with guest-loading crystalline phase transformation from initial nonporous phases to porous guest-containing phases induced by vapor sorption; (c) the selectivity is generally derived from the relative thermodynamic stabilities among the guest-loaded crystalline structures upon guest uptake; (d) reversible transitions between

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[1–29] J.-R. Wu, Prof. Y.-W. Yang
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, International Joint Research Laboratory of Nano-Micro Architecture Chemistry (NMAC), College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012 (P. R. China)
E-mail: yyang@jlu.edu.cn
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/anie.202006999.
guest-free and guest-containing crystalline structures make NACs of pillararenes highly recyclable.

While the properties and applications of the robust pillararenes-based NACs are well-established,[19–21] new NACs based on pillararene derivatives and other important synthetic macrocycles, such as biphen[3]arene,[22] leaning pillar[6]arene (i.e., leaning tower[6]arene),[23] geminiarene,[24] bowtiearene,[25] cucurbit[6]uril,[26] hybrid[3]arene,[27] and tia[5]arene[28] have been developed and recently reported. In this Minireview, we describe some important progress in the development of synthetic macrocycles-based NACs, especially the constructions of NACs from newly discovered macrocyclic arenes for molecular separation and vaporchromic application in the last two years.

2. Separation of Haloalkene Cis–Trans Isomers

The separation of mixed haloalkene cis–trans isomers is of great significance in the petrochemical industry as each isomer has its particular application and must be used separately in most chemical and industrial cases.[19] However, their similar boiling points make them practically difficult to separate by traditional distillation, and fractional distillation with very high towers and operating cost is also not a long-term solution for sustainability.

Recently, Li and co-workers reported the first example of NACs based on biphen[3]arene H1 (Figure 1a),[24] capable of separation of cis- and trans- 1,2-dichloroethene (cis-DCE and trans-DCE) isomers. Adaptive H1 crystals (H1a) could adsorb cis-DCE from a 1:1 (v/v) cis-trans-DCE isomers mixture with a purity of 96.4%. Single crystal structure and powder X-ray diffraction (PXRD) analysis confirmed that a structural transition from H1a to the cis-DCE-loaded structure (cis-DCE:H1) occurred during the adsorption of cis-DCE (Figure 1b), while in sharp contrast, no obvious changes were observed after H1 was exposed to trans-DCE vapor. These results indicated that the cis-trans selectivity was derived from the relative stability of cis-DCE:H1 crystal in comparison with original H1a and trans-DCE-loaded one. Moreover, H1a could be reconstructed by heating and still possess the capability in selective separation of cis- and trans-DCE isomers mixture for many times without loss of performance, representing a new non-pillararene NAC for separation.

Huang and co-workers investigated the separation of cis- and trans- 1,4-dichloro-2-butene (DCB) isomers by NACs of perethylated pillar[5]arene H2 and perethylated pillar[6]arene H3 (H2a and H3a as NACs) (Figure 2a,b).[29] Both H2a and H3a showed uptake of each single-component DCB isomer with gate-opening behaviors, but the uptake process only transformed H3a into highly differentiated host-guest binding structures (trans-DCB:H3 and 2(cis-DCB):H3), implying the great potential of H3a in separating DCB cis- and trans-isomers. In trans-DCB:H3, H3 molecules assembled into an infinite angle-to-angle 1D channel structure, and one trans-DCB molecule was hosted in the center of per H3 molecule, giving an overall 1:1 host-guest complex (Figure 2c). In terms of 2(cis-DCB):H3, H3 molecules exhibited a window-to-window packing mode with honeycomb-like 1D channels, where two cis-DCB molecules were located in per H3 cavity in parallel to each other, rendering an overall 1:2 host-guest assembly (Figure 2d). Upon exposure to a 1:1 (v/v) mixture of DCB cis-trans-isomers vapor, H3a only adsorbed trans-DCB with the structural transformation to trans-DCB:H3, suggesting a good selectivity toward trans-DCB (Figure 2e). Upon heating, trans-DCB molecules could be released from trans-DCB:H3 with a purity of over 97%, and the crystalline phase could be reconstructed into the original H3a and reused many times without losing performance. In comparison, H2a showed a low selectivity in discriminating DCB cis- and trans-isomers.

3. Separation of Monochlorotoluene Isomers

Monochlorotoluene, particularly p-chlorotoluene (PCT), is an important starting material, additive, and intermediate in the production of pesticides, medicines, dyestuffs, and so
PCT is prepared industrially by the reaction of liquid toluene with chlorinating agents through the process of electrophilic substitution. Generally, a mixture of o-chlorotoluene (OCT) and PCT, together with a small amount of m-chlorotoluene (MCT) and aromatic hydrocarbons with varying degrees of chlorination, could be obtained in the products.

Thus, the separation of PCT and OCT is the key step to obtain individual isomers with high purity. However, due to the very close high boiling points (PCT: 435.5 K, OCT: 432.1 K), PCT and OCT are currently separated by the cumbersome and energy-inefficient method, that is, distillation-crystallization.

Recently, Huang and co-workers reported the highly selective separation of PCT from OCT by the NACs of \( \text{H}_2 \) and \( \text{H}_3 \). \( \text{H}_2 \) and \( \text{H}_3 \) adsorbed PCT with gate-opening behaviors (xx: \( P/P_0 = 0.7 \), xx: \( P/P_0 = 0.8 \)). Trace amount of OCT was found to be absorbed in, even under a relatively high pressure (\( P/P_0 = 1.0 \)) (Figure 3a,b), which indicated the capability of \( \text{H}_2 \) and \( \text{H}_3 \) in distinguishing PCT and OCT isomers. Upon exposure to a mixture of PCT and OCT vapor, \( \text{H}_2 \) and \( \text{H}_3 \) adsorbed only PCT with the crystalline phase transitions to PCT-loaded forms (3(PCT)\( \subset \)2(H2) and PCT\( \subset \)H3) (Figure 3c). Upon heating, PCT molecules can be released from 3(PCT)\( \subset \)2(H2) and PCT\( \subset \)H3 in a purity of 99.1% and 96.1%, respectively, implying a remarkable PCT selectivity in both NACs of \( \text{H}_2 \) and \( \text{H}_3 \). Furthermore, they also discovered the gate-opening behavior of \( \text{H}_2 \) changes at different temperatures upon exposure to various fractions of PCT/OCT mixtures, which is very helpful for the understanding of the thermodynamic mechanisms of NACs in molecular separation applications.

4. Separation of Chloropyridine Isomers

2-Chloropyridine (2-CP) is a very important feedstock in chemical industry, and has been widely used in pesticide synthesis, medicine, synthetic chemistry, etc. In industry, 2-CP is always produced from the chlorination of pyridine at high temperatures (260 to 420°C). However, 3-chloropyridine (3-CP) and other multi-substituted chloropyridines are inevitably produced and mixed in the reaction products. Multi-substituted by-products can be easily removed by fraction in virtue of their large boiling point differences in comparison with 2-CP. However, the separation of 2-CP and 3-CP by rectification is very difficult as a result of their similar boiling points. Therefore, selective separation methods are highly desirable.
points and molecular sizes. Thus, it is of great significance to exploit energy-efficient, cost-effective, and simpler processes for 2-CP/3-CP isomers separation.

Recently, Huang and co-workers investigated the separation of 2-CP/3-CP isomers using NACs of H2, H3, perbromoethylated pillar[5]arene (H4), and perbromoethylated pillar[6]arene (H5) (Figure 4a),[22] which are different in substituents and cavity size. Solid-vapor adsorption experiments confirmed that only NACs of H5 (H5a) could separate 2-CP from a 2-CP/3-CP equimolar mixture with a purity of 96.4% upon heating (Figure 4b). Single crystal structure in conjunction with PXRD analyses demonstrated that the selectivity came from the different host-guest interactions and stabilities between 2-CP- and 3-CP-loaded H5 structures, i.e., 2(3-CP)⊂H5 and 2(2-CP)⊂H5 (Figure 4c), and the poor selectivity of H2, H3, and H4 was ascribed to the similar host-binding modes and spatial structures after adsorption of 2-CP and 3-CP, respectively. Moreover, the original H5a could be easily reconstructed by heating, and reused multiple times without losing its performance in selectivity and capacity. This work represents the first example of NACs for application in the separation of aromatic heterocyclic isomers.

5. Toluene/Pyridine Separation

Toluene (Tol) is a high-value feedstock both in petrochemical industry and synthetic chemistry, and also commonly used as solvent, starting material, and intermediate in the production of pesticide, dyes, explosives, polyesters, explosives, synthetic resins, etc.[39] In industry, Tol is prepared by the coal coking process and often mixed with a small percentage of pyridine (Py). However, the separation of Tol and Py by conventional distillation is practically impossible due to their similar boiling points (Tol: 110.8°C, Py: 115.2°C) and the formation of minimum-boiling azeotrope. The present separation technologies for Tol/Py include azeotropic distillation, extractive distillation, and pressure-swing distillation,[40] but these approaches are energy intensive and must be utilized with additional organic entrainers, causing environmental pollution apart from high capital and operating costs. Thus, the exploration of energy-efficient and easy-to-operate strategies for Tol/Py separation is needed.

Kim and co-workers discovered that cucurbit[n]uril crystals with permanent porosity can serve as adsorptive materials for gas storage and separation in their early reports.[41] Very recently, Huang and co-workers demonstrated that cucurbit[n]urils can also be used to construct NACs in addition to permanently porous crystals.[23] They found that NACs of cucurbit[6]uril (H6) could work as an effective adsorbent for separation of Tol/Py mixture (Figure 5a), no matter through the processes of solid-vapor phase or solid–liquid phase adsorption. Quite similar to pillararenes-based NACs, upon exposure to a 1:1 (v:v) mixture of Tol/Py, adaptive H6 crystals (H6a) selectively adsorbed Py, resulting in a structural transition from H6a to a Py-loaded form (Py⊂H6) (Figure 5b). Gas chromatography (GC) showed that the purity of Py reached nearly 100% upon release from Py⊂H6. Interestingly, the purity of Py still retained as high as 93.4%, even when the mixture ratio of Tol and Py was 100:1 (v:v), further implying the high selectivity of H6a toward Py and its great potential in industrial use for Tol purification. Moreover, the removal of Py transformed the crystalline phase of Py⊂H6 back to H6a, which could be reused multiple cycles without loss of performance. This work provides the
first example of cucurbit[n]urils-based NACs for application in molecular separation.

6. Separation of Haloalkane Isomers

Haloalkanes are very important feedstocks in both petrochemical industry and scientific research, and have been widely used not only as solvents, starting reagents, and intermediates in organic synthesis, but also as raw materials in industry to produce lubricants, pesticides, refrigerants, etc.[42] In industry, linear and branched haloalkanes isomers are usually produced simultaneously and coexist in the reaction products,[43] which must be separated. However, the separation of haloalkanes isomers using conventional methods is energy intensive and environmentally unfriendly due to their similar physical properties. Moreover, due to their slight differences in structure, the use of porous materials for selective separation of haloalkane isomers have rarely been reported thus far.

In 2018, Huang and co-workers first described the separation of 1-chlorobutane (1-CB) from an equimolar mixture of 1-chlorobutane and 2-chlorobutane (2-CB) with a purity over 99%.[7] Very recently, we reported that NACs (H7a) of perethyalted leaning pillar[6]arene (H7) had the ability of separating 1-2-bromoalkanes isomers (Figure 6a).[25b] H7a could adsorb all the six single-component linear and branched isomers including 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), and was transformed to two different groups of host-guest assemblies, i.e., 1-bromalkanes-loaded forms (1-BPR·H7, 1-BBU·H7, and 1-BPE·H7) and 2-bromalkanes-loaded forms (2-BPR·H7, 2-BBU·H7, and 2-BPE·H7) (Figure 6b). In the 1-bromalkanes-loaded structures, H7 molecules are highly tilted, each 1-bromalkane molecule was sandwiched between two subunits of adjacent H7 molecules, stabilized by multiple C–H⋯π interactions (Figure 6c). In contrast, H7 showed an interesting guest-induced conformation change in the 2-bromalkane-loaded crystals, with a deformed hexagonal structure (Figure 6d). But only 2-BPR can be stably trapped in the cavity of H7 via moderate in-cavity host–guest interactions. Upon exposure to three groups of 1:1 (v/v) mixtures of 1/2-bromalkanes isomers vapors, H7a selectively adsorbed 1-bromalkanes (1-BPR, 1-BBU, and 1-BPE) over its 2 positional isomers, leading to the crystalline phase changes to 1-BPR·H7, 1-BBU·H7, and 1-BPE·H7, respectively. This selectivity generally comes from the different binding modes and different stabilities of 1-bromalkanes- and 2-bromalkanes-loaded H7 crystals as aforementioned. The purities of 1-BPR, 1-BBU, and 1-BPE can be improved from 50% to 89.6%, 93.8%, and 96.3% in only one adsorption cycle after release from 1-BPR·H7, 1-BBU·H7, and 1-BPE·H7, respectively (Figure 6c). Meanwhile, the removal of 1-bromalkanes transformed the host-guest complexes back to H7a, making H7a highly recyclable (Figure 6f). This is the first example of leaning towerearene-based NACs for application in isomers separation.

Afterward, the removal of trace CB isomers using NACs of H2a and H3a to produce 1-CB and 2-CB of high grade (Figure 7a) was achieved by Huang and co-workers.[36] H2a removed trace 1-CB (2%) from 2-CB (98%) to enhance its purity to 99.9% (Figure 7b), on the contrary, H3a could remove trace 2-CB (2%) from 1-CB (98%) to improve its purity up to 99.9% (Figure 7c). This opposite selectivity of H2a and H3a was derived from the thermostability of the newly formed CB-loaded crystal structures (1-CB·H2 and 2-CB·H3) after adsorption was higher than its corresponding isomer-loaded forms, respectively.

7. n-Hexane Purification

The production of alkanes is of great significance in the petrochemical industry and synthetic chemistry. n-Hexane (nHex), as a broad-spectrum n-alkane is widely used in the fields of scientific research, industrial extraction, pharmaceutical and food industry, etc.[44] In industry, nHex is produced by distillation of raffinate oils (6# solvent oil,
composed of C6 alkane mixtures), and often mixed with a small proportion of other C6 impurities, which must be further removed to obtain nHex of high grade. However, the boiling points of nHex and methylcyclopentane (Mcp) are very close (nHex: 68.7°C, Mcp: 71.8°C) and the separation of nHex from Mcp by conventional distillation is unrealistic. The dominant industrial methods for production of high-purity nHex are azeotropic distillation and extractive distillation, which are always accompanied with high operating costs and complex processes.

In 2015, Ogoshi and co-workers found that NACs of H2a can adsorb n-alkanes containing five or more carbon atoms with gate-opening behaviors, and n-Hex can transform H2a to a herringbone solid-state host-guest assembly. For comparison, branched, cyclic alkanes and n-alkanes with fewer than four carbons cannot be adsorbed by H2a. Shortly afterwards, the separation of n-alkanes with different chain lengths by the NACs of H2a, and the selective removal of isooctane from different ratios of n-heptane/isoctane mixtures to increase the research octane numbers (RONs) by the NACs of H3a were also achieved by the same group. Inspired by these pioneering works, we investigated the separation of nHex/Mcp by the NACs of H7a. Our results indicated that H7a could selectively adsorb n-Hex from a 1:1 (v:v) mixture of nHex/Mcp through the processes of both solid-vapor and solid-liquid phase adsorption, leading to a structural transition from H7a to a nHex-loaded complex (nHexتش7). As illustrated in nHexتش7, the adsorbed nHex molecules were located in the extrinsic pores between two adjacent H7 molecules via the stabilization of multiple C–H···π interactions. GC experiments showed that the purity of nHex could reach nearly 97% after release from nHexتش7. Intriguingly, the high selectivity of H7a toward nHex still remained in relatively complex C6 alkane/cyclanes mixtures (Figure 8a-c). Quite different from traditional porous materials which usually rely heavily on their suitable pore shape and size in the separation of alkanes, this selectivity of H7a was derived from the different thermodynamic stabilities of nHexتش7 and other C6-loaded H7 crystals.

8. Aromatics/Cyclic Aliphatics Separation

In the chemical industry, cyclic aliphatics are commonly produced by hydrogenate their corresponding aromatics. The unreacted aromatics are inevitably mixed in the raw cyclic aliphatics products, and must be separated. However, the very similar physical properties of aromatics and their
corresponding cyclic aliphatics make the separation difficult to achieve via conventional distillation. For example, the slight difference in boiling points (0.6 K) between benzene (Bz) and cyclohexane (Cy) classifies them as one of the most difficult chemical separations in petrochemical industries. Thus, highly selective adsorbents for aromatics/cyclic aliphatics separation are highly desired and in urgent need.

In 2018, Huang and co-workers reported the use of NACs of H2a and H3a to separate aromatics and cyclic aliphatics. For example, the slight difference in boiling points (0.6 K) between benzene (Bz) and cyclohexane (Cy) classifies them as one of the most difficult chemical separations in petrochemical industries. Thus, highly selective adsorbents for aromatics/cyclic aliphatics separation are highly desired and in urgent need.

Later in 2019, Sue and co-workers described the first example of Bz/Cy fractionation by using NACs of a newly designed macrocyclic arene named tiara[5]arenes H8 (Figure 9a).[21] Upon exposure to a mixture of Bz/Cy (1:1 v/v), NACs of H8 (H8a) selectively adsorbed Bz over its hydrogenated product Cy, resulting in a structural transition from H8a to a Bz-loaded form (Bz%H8). Instead of forming host-guest inclusion complexes in Bz%H8, H8 molecules with a distorted conformation assembled 2D channels to accommodate the adsorbed Bz molecules. Upon heating, Bz molecules were released from Bz%H8 with a purity of 92.3%, and H8a could be recovered for repeated separation cycles without losing performance (Figure 9b).

Although H8a possesses the capability in separating Bz and Cy, the selectivity is modest, far away from the practical demands in industry. Soon afterwards, Huang and co-workers found that NACs of another newly designed macrocyclic arene, namely hybrid[3]arene H9 (Figure 10a),[28] can also serve as an effective adsorbent for selective separation of Bz/Cy mixture. NACs of H9 (H9a) could adsorb single-component Bz vapor with gate-opening behavior (P/P0 = 0.6), and the adsorbed Bz was barely released at the beginning of the desorption process. By contrast, trace amount of Cy was adsorbed even in a relative high pressure (P/P0 = 1.0) (Figure 10b). These results indicated that H9a displayed a good performance in adsorption and storage of Bz rather than Cy. Similar to H8a, H9a selectively adsorbed Bz upon exposure to an equimolar mixture of Bz/Cy vapor, and leading to the structural transition to a Bz-loaded form (Bz%H9). As shown in Figure 10c, distorted H9 molecules were assembled into infinite channels, and Bz molecules hosted in these extrinsic pores via the stabilization from multiple C–H···O and C–H···π interactions. In comparison with H8, Bz molecules trapped in Bz%H9 could be released with a relative high purity of 97.5%, and the reactivated H9a could still separate Bz/Cy mixture for more than ten times without losing performance.

In 2019, we reported the first example of dual-selective NACs based on our newly designed and synthesized macrocyclic arene, namely geminiarene H10 (Figure 11a).[26a] By combination of the subunit connection modes of pillararenes (para-positional connection) and calixarenes (meta-positional connection), H10a could selectively adsorb Bz and Cy with gate-opening behavior (P/P0 = 0.6), and the adsorbed Bz and Cy were barely released at the beginning of the desorption process. By contrast, trace amount of Bz was adsorbed even in a relative high pressure (P/P0 = 1.0) (Figure 11b). These results indicated that H10a displayed a good performance in adsorption and storage of Bz and Cy rather than Cy. Similar to H8a and H9a, H10a selectively adsorbed Bz and Cy upon exposure to an equimolar mixture of Bz/Cy vapor, and leading to the structural transition to a Bz/Cy loaded form (Bz%H10). As shown in Figure 11c, distorted H10 molecules were assembled into infinite channels, and Bz and Cy molecules hosted in these extrinsic pores via the stabilization from multiple C–H···O and C–H···π interactions. In comparison with H8 and H9, Bz and Cy molecules trapped in Bz%H10 could be released with a relative high purity of 97.5%, and the reactivated H10a could still separate Bz/Cy mixture for more than ten times without losing performance.
connection). H10 presented two totally different but indeed interconvertible molecular configurations in the solid-state, one like the conformation of pillarenes (H10a) and another like cone-shaped calixarenes (H10b) (Figure 11 b,c). By virtue of the dual conformational feature, we found that H10a and H10b possess the capability in sorting mixture of chlorobenzene (CB) and chlorocyclohexane (CCH) with directly opposite selectivity. H10a selectively adsorbed CCH over CB through the process of solid–liquid contact adsorption, while H10b selectively separated CB from CCH via solid-vapor adsorption, resulting structural transformations from H10a and H10b to CCH and CB-containing forms (4- (CCH)<H10 and CB< H10) (Figure 11 d,e), respectively. Meanwhile, both H10a and H10b can be recovered by heating and recycled many times without any loss in selectivity and capacity. Interestingly, H10b could separate both CB and CCH with over 97% and 87% purities via the method of solid–liquid adsorption in just only one separation cycle (Figure 11 f). This dual selectivity arises from the successive phase transitions from H10b to CB< H10, followed by CB< H10 to 4(CCH)< H10. Thus, giving credit to the guest-loading and displacing processes in accompany with the phase changes, CB and CCH molecules could be separated in order by H10b. This work represents the first example of NACs with reversible selectivity in molecular separation.

9. Vapochromic Supramolecular Systems

The development of vapochromic materials is of great significance in both scientific research and practical applications, as it can be used as sensors to detect specific vaporized molecules through the color changes of solid materials[40]. In 2017, Ogoshi and co-workers reported the first example of vapochromic behavior of NACs using pillar[5]arene-[1]quinone H11.[9] Guest-free H11 crystals (H11a) has the capability in discriminating n-alkane over branched or cyclic alkane vapor with a color change from brown to red (Figure 12 a), implying an alkane-shape-selective vapochromism. Besides, another vapochromic behavior with the color change from brown to black was also observed upon exposing H11a to methanol vapor. The mechanism of these color changes generally arises from the different charge-transfer interactions brought by highly differentiated π-stacking arrangements among the guest-free and guest-containing crystals, thus leading to color changes after vapor uptake. Then, Huang and co-workers described the adsorption and sensing of linear volatile aliphatic aldehyde by the NACs of H11a,[39] that is to say, H11a could adsorb vaporized aldehyde with different carbons in accompany with different color changes.

Giving credit to the highly active benzoquinone subunit in H11, Huang and co-workers also reported a post-synthetic modification procedure of H11a by direct contact with amine vapors.[38] In this approach, amine vapors were physically adsorbed in the cavity of H11 first, then slowly reacted with its adjoining benzoquinone subunits through Michael addition, and finally making new compounds as well as new crystalline structures generated in situ (Figure 12 b). Thus, vapochromism in this procedure was derived from the conjugation of physical adsorption and chemical reaction, occurrence one after another. Furthermore, this procedure also presented selectivity of both reactant shape and size as a result of the rigid cavity and binding preference of H11.

Afterwards, the same group described the first example of vapor-induced fluorochromic NACs based on an anthracene-containing pillar[5]arene derivative H12.[3] Upon exposure to different ketone vapors, activated H12 crystals (H12a) displayed fluorochromism with alkyl length selectivity. As illustrated in Figure 13 a, H12a adsorbed C4-C6 ketones vapors with obvious blue shift in fluorescence, by contrast, C7 and C8 ketones could not trigger obvious fluorescence change. Single crystal structures in conjunction with PXRD analysis demonstrated that the mechanism of fluorochromism of H12a came from the different aggregation modes of anthracene group (H-aggregation or J-aggregation) upon guest uptake (Figure 13 b). In other words, the blue-shifted fluorescence emission was mainly caused by guest-induced crystalline phase transformation, accompanied with the transition of H-aggregated anthracene excimer into J-aggregationated anthracene monomer in the H12 crystals.

Very recently, Cong and co-workers also reported a stimuli-responsive fluorochromic NACs based on a newly designed macrocyclic arene, bowtiearene H13 (Figure 14 a).[27] which processes a Figure-of-eight molecular configuration with dual binding cavity in one molecule. The fluorochromism of H13 could be triggered by both mechanic force and xylene vapors. As shown in Figure 14 b, mechanic force can destroy the ordered arrangement of H13 in crystals, inducing a significant red-shift in fluorescence emission and an increase of the lifetime. Conversely, p-xylene can recover the ordered molecular arrangement as well as the crystallinity of the ground powder by vapor uptake, thus resulting in a blue-shifted fluorescence emission and a decrease of the lifetime.

Figure 12. (a) Crystal structures of H11 prepared from n-hexane and methanol and photographs showing color changes of H11a upon being exposed to different vapors. Reproduced with permission from ref. [25]. Copyright 2017, American Chemical Society (b) Schematic representation of the post-synthetic modification in H11a by capturing butylamine vapor. Reproduced with permission from ref. [49]. Copyright 2018, American Chemical Society.
Based on these results, the $\text{H13}$-loaded paper can be written and erased multiple times upon treatment of mechanical force and vapor fuming (Figure 14c), which not only proved the high recyclability and stability of the fluorochromism of $\text{H13}$, but also suggested a potential sensing material for intended practical applications.

10. Summary and Outlook

In summary, this Minireview summarizes the recent advances of synthetic macrocycle-based NACs for molecular separation and vapochromic supramolecular systems. Giving credit to multifarious macrocycle platforms, including but not limited to pillarenes, biphen[3]arene, leaning pillar[6]arene, geminiarene, bowtiearene, cucurbit[6]uril, hybrid[3]arene, and tiara[5]arene discussed here, NACs can work at the supramolecular level and display great potentials in discriminating molecules, especially those with slight differences in size, shape, and boiling point in practical petrochemical production. However, some existing weak points need to be solved or strengthened along the rapid development of NACs, which are listed as follows: (i) most guest-free structures of macrocycles-based NACs have not been accurately defined by X-ray single crystal diffraction except pillarenes and geminiarene till now, limiting the in-depth investigations in structure-function relationship and making the most applications of NACs established by continuous attempts rather than reasonable prediction; (ii) all of the reported experiments were carried out on a milligram scale or gram scale at most, thus it’s imperative to fine-tune the existing system or exploit commercial-scalable NACs to meet the practical demands in industry; (iii) the recovery process of the purified substrates is still an unresolved issue under the affluent separation applications of macrocycles-based NACs. In the meantime, the general mechanism of the structural transformations between different forms of solvates of these macrocycles should be ruled out with the aid of computational chemistry, where crystal structure prediction may potentially offer more insight into these systems and can be very helpful to the design of these type of materials. No matter what, we strongly believe NACs could be a kind of disruptive adsorption/separation materials in the foreseeable future, and the investigation of synthetic macrocycle-based NACs is very necessary and of great importance to synthetic chemistry, supramolecular chemistry, materials science, and separation technology, therefore it will not only exert valuable influence on basic scientific research but also gives conceptual materials for intending applications.

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Conflict of interest

The authors declare no conflict of interest.


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