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Adsorptive separation of *para*-xylene by nonporous adaptive crystals of phenanthrene[2]arene⁺

Ying Hou, Yin-Rong Duan, Man-Hua Ding,* Lin-Li Tang and Fei Zeng 🕑 *

In this work, we developed a new method for the preparation of phenanthrene[2]arene on a large-scale. Meanwhile, the synthetic phenanthrene[2]arene has been successfully used as nonporous adaptive crystals for the separation of *para*-xylene (**pX**) from xylene isomers. The crystal structure revealed that one host molecule can adsorb one **pX** molecule to form the **1@pX** complex, in which **pX** is located in the cavity of the host.

Xylene is an aromatic hydrocarbon in which two hydrogen atoms on the benzene ring are replaced by two methyl groups, so it has three isomers: ortho-xylene (oX), meta-xylene (mX), and para-xylene (pX). Xylene isomers are important chemical feedstocks in the petrochemical and pharmaceutical industries and used for the production of many polymers, plastics, fibers, solvents, and fuel.1-7 However, most xylenes used in industry are single-component compounds. Therefore, the prepared xylene mixtures need to be individually separated in most cases. The separation of the xylenes was classified as one of the "seven chemical separations to change the world" due to their similar kinetic sizes, close boiling points, and the same molecular weight.⁸ The boiling point of oX is relatively high (417.55 K) and can be separated by rectification, while the slight difference in boiling points (only 0.8 K) between pX (411.45 K) and mX (412.25 K) makes them almost impossible to separate via a traditional distillation process. However, pX could be isolated by fractional crystallization due to its relatively higher melting point compared with mX.9 However, the energy requirement for fractional crystallization is high because of the need to cool large quantities of material to about -53 °C. Therefore, it is necessary and desirable to develop easy operation and more energy efficient methods to separate pX and mX.

In the past decades, a number of methods have been developed to meet the separation challenge of xylene isomers, including solvent extraction¹⁰⁻¹⁶ and adsorption by porous materials.¹⁷⁻²¹ The method of solvent extraction sometimes has the highly toxic effect on the environment and strong corrosive effect on the equipment impeded its long term applicability. While, the adsorption by porous materials are built using reversible chemistry and have comparatively low

moisture or thermal stability, which restrict their further application in industrial. Recently, macrocycle-based nonporous adaptive crystals (NACs) have attracted considerable interest as they display great potentials for practical applications, especially in the adsorption, separation, and storage of hydrocarbons.²²⁻³¹ Huang and coworkers reported the separation of **pX** from its structural isomers, *mX* and *oX* by nonporous adaptive crystal of pillar[6]arene with a purity of 90%.³² Khashab's group also achieved the separation of **pX** using a polymorphic azobenzene cage.³³ Since the discovery of crown ethers by Pedersen in 1967, supramolecular chemistry has been developed for many years and a series of macrocyclic hosts have been designed and synthesized.³⁴⁻⁴² However, they have been studied as xylene isomers selective adsorbents only rarely.⁴³⁻⁴⁵

The development of NACs with high pX adsorption capacity and separation purity is still a challenging work. Herein, we report that phenanthrene[2]arene **1** can be used as a host for the encapsulation and separation of pX from the equimolar mixture of pX and mX in the vapor phases through shape selective crystallization under mild and user-friendly conditions. Furthermore, **1** exhibits excellent recyclability, with no significant decrease in performance after seven cycles of adsorption and desorption (Fig. 1).



Fig. 1 Structural representation of the capture of pX from a pX/mX mixture using phenanthrene[2]arene crystals.

Department of Biology and Chemistry, Hunan University of Science and Engineering, Yongzhou 425199, China. E-mail: zengfei@iccas.ac.cn; 42979930@qq.com

[†] Electronic supplementary information (ESI) available: Synthesis of 2 and 3; The ¹H and ¹³C NMR spectra of 2 and 3. CCDC 2165484 for 1@*pX*, 2175792 for 1@*mX*. For ESI and crystallographic data in CIF or other electronic format see https://doi.org/10.1039/d2ra03773d

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Although, the synthesis of host **1** (ref. 46) have been reported by our group recently. However, we found that the synthetic route can be further optimized to synthesis of the precursor **3**, which is beneficial to the subsequent large-scale production. As shown in Scheme **1**, starting from the commercially available **3**,6-dibromophenanthrene-9,10-dione and **2**,5-dimethoxyphenylboronic acid, compound **3** can be quantitatively obtained after work up by simple suction filtration by the Suzuki coupling reaction. Then, the precursor **2** can be quantitatively obtained from compound **3** through sodium dithionite reduction and methylation with dimethyl sulfate.

Similar to the phenanthrene[2]arene as the nonporous adaptive crystals for benzene adsorption capacity,⁴⁶ activated host **1** was prepared by recrystallization in the mixture of $CH_2Cl_2/MeOH$ and dried under vacuum at 150 °C for 6 h. To study the selectivity of **pX** over **mX**, single-component solid-vapor sorption experiments were first performed with the activated solid of **1** toward **pX** and **mX**. The mole ratio of time-dependent solid-vapor sorption plots were determined by the ¹H-NMR analysis. As shown in Fig. 2a, the adsorption capacity of **1** toward **pX** in the first four hours was negligible, but the adsorption capacity of **pX** increased significantly with time and it required about 16 hours to reach saturation. The uptake of **pX**



a) a) b) b)

Fig. 2 (a and b) Time-dependent solid-vapor sorption plots of 1 for single-component vapour pX and mX respectively; (c and d) thermogravimetric analysis of 1 after sorption of pX or mX adsorbed vapor for 20 h.

was calculated to be about one *p*X/1 at saturation. Similar to the pX, activated 1 also showed adsorption capacity toward mX. However, it takes even more time for the adsorption capacity of mX to increase significantly (Fig. 2b). The uptake of mX was calculated to be about 1.2 mX/1 at 20 hours. These results suggest that both pX and mX can be adsorb by the activated solid 1 and the absorption is a relatively slow process. Consistent with the single-component adsorption experiments, TGA analysis further confirmed the absorb number of 1 toward pXand mX. Upon heating the activated 1 that adsorbed pX or mX vapor for 20 hours, a weight loss of 9.2% from 53 to 188 °C and a weight loss of 10.8% from 48 to 145 °C were observed, which corresponded to the release of one pX molecule or 1.2 mX molecules per host 1, respectively (Fig. 2c and d). The higher release temperature of pX than mX revealed that pX could be more steadily stored in 1 crystals than mX.

To get more information about adsorption capacity of 1 toward pX and mX, We tried to get the single crystals of 1 loaded with *pX* or *mX*. Single crystal structures that suitable for X-ray analysis were obtained by slow evaporation of the solution of 1 in pX or mX, providing unambiguous evidence for the formation of 1@pX and 1@2mX. As shown in Fig. 3a, the resulting crystal structure revealed that one host molecule 1 can adsorbs one pX molecule to formation of 1@pX complex, in which pX located in the cavity of host. Interestingly, CH···H and CH··· π interactions between *p***X** and host **1** with the distance of 2.398 Å (a) and 2.865 Å (b) were observed. Because of these multiple noncovalent interactions, the host 1 showed high adsorption capacity for pX. Moreover, it was found that one host molecule 1 can adsorbs two mX molecules to formation of 1@2mX complex (Fig. 3b), in which two mX molecules not located in the cavity of host. Additionally, CH···O and CH··· π intermolecular interactions also exist between the mX and host 1, and their distance are measured to be 2.624 Å (c) and 2.760 Å (d), respectively. From the b-axis direction of 1@pX and 1@2mX complex packing structure (Fig. 3c and d), a large number of pX and mX molecules are absorbed in the crystal structure. These results further support the adsorption capacity of 1 toward pX



Fig. 3 Crystal structure of (a) 1@pX; (b) 1@2mX; (c) and (d) packing of 1@pX and 1@2mX, view along the *b* axis.

and mX provides us an opportunity to use host 1 as NACs material for the separation of pX and mX. Moreover, the PXRD pattern of activated solid 1 after absorbing pX showed a significant change in comparison with the original pattern of activated 1, which suggested the structural transformation of activated 1 upon capture of pX vapour (Fig. S8†). The PXRD pattern of activated solid 1 after absorbing mX showed a no change in comparison with the original pattern of activated 1, which suggested no structural transformation of activated 1, which suggested no structural transformation of activated 1 upon capture of mX vapour (Fig. S9†). In addition, the PXRD pattern of activated 1 after capturing pX was matched well with the simulated patterns based on single-crystal structures of 1@pX. This indicated that activated 1 transformed into 1@pX after adsorption of pX.

Based on the different sorption ability of activated 1 toward pX and mX, we wondered whether 1 could separate pX/mXmixtures. To confirm this hypothesis, we performed twocomponent (1:1 ratio) competition sorption experiments. Similar to the single-component solid-vapor sorption experiments, the adsorption capacity of 1 toward pX/mX mixtures in the first three hours was negligible. However, after 3 h, pX could be predominantly adsorbed over mX (Fig. 4a). At saturation, ca. 0.83 pX molecules were adsorbed with 0.18 mX molecules per activated 1 from the ¹H-NMR analysis (Fig. S10[†]). This result indicates that activated 1 has selective adsorption of pX. The Gas chromatography determined the percentage of pX adsorbed by activated 1 to be 81% (Fig. 4c). In addition the powder X-ray diffraction patterns of activated 1 that adsorbed pX/mX mixtures were almost the same with the simulated patterns based on single-crystal structures of 1@pX (Fig. 4b), indicating



Fig. 4 (a) Time-dependent solid-vapor sorption plot of activated 1 for pX and mX equimolar mixture vapor. (b) PXRD patterns of 1: (I) activated 1 adsorption of pX vapour for 20 h; (II) activated 1 adsorption of mX vapour for 20 h; (III) activated 1 adsorption of pX/mX mixture vapour for 20 h; (IV) activated 1 after adsorption of pX/mX mixture vapour for 20 h and then heating at 150 °C under vacuum for 3 h; (V) simulated from single-crystal structure of 1@pX/mX mixtures for 20 h as measured by activated 1 that adsorbed pX/mX mixtures for 20 h as measured by gas chromatography. (d) Relative uptakes of pX and mX by activated 1 that adsorbed pX/mX mixtures for 20 h after seven recycles.

the similar pX loaded 1 crystals formed. Although, in the crystal structure of 1@2mX, one host molecule can adsorbs two mX molecules, but the host 1 exhibits better pX selectivity over mX, probably due to better matching of pX in the intrinsic cavity of host 1. Considering the further application in real production, recycling capacity is an important criterion for assessing an adsorbent. ¹H NMR spectroscopy and TGA analysis revealed that, by heating 1@pX at 150 °C in vacuum for 3 hours, the absorbed pX could be completely released (Fig. S13 and S14†). We also proved that the newly formed crystals were activated 1 as indicated by PXRD (Fig. S15†). Moreover, the re-activated solids can be re-used in next adsorption cycles and no obviously loss of selectivity or capacity were observed after recycling seven times (Fig. 4d).

Conclusions

In summary, we developed a new method for the large-scale preparation of phenanthrene[2]arene **1** and demonstrated that phenanthrene[2]arene can be used for the adsorption and separation of industrially important xylene isomers. The activated crystals of **1** showed higher pX adsorption capacity than mX. One host molecule can at maximum adsorb one pX molecules in its central cavity. Moreover, activated crystals **1** also exhibits excellent recyclability when used as NACs materials to separation of pX and mX. The advantages of simple synthesis, high separation efficiency, and outstanding recycling performance of **1** makes this material possesses enormous potential for applications in the chemical industry.

Conflicts of interest

There are no conflicts to declare.

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