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## Molecular recognition and adsorptive separation of *m*-xylene by trianglimine crystals<sup>†</sup>

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The separation of xylene isomers is one of the most challenging tasks in the petrochemical industry. Herein, we developed an efficient adsorptive molecular sieving strategy using crystalline trianglimine macrocycle (1) to separate the elusive *m*-xylene isomer from an equimolar xylenes mixture with over 91% purity. The selectivity is attributed to the capture of the preferred guest with size/shape selectivity and C-H… $\pi$  interactions. Moreover, the trianglimine crystals are readily recyclable due to the reversible transformation between the guest-free and guest-loaded structures.

The energy intensive separation and purification of petrochemical isomers currently consumes 10–15% of the world's total energy production. Separation of  $C_8$  aromatics, *o*-xylene (OX), *p*-xylene (PX), *m*-xylene (MX) and ethylbenzene (EB), is considered as one of the 'seven chemical separations that will change the world.<sup>1</sup> Xylenes are obtained from crude oil by catalytic reforming and pyrolysis of gasoline. Each of the isomers is an important building block in the production of polymer fibers, films, plasticizers, resins, *etc.*<sup>2–4</sup> Separation of MX from a mixture of OX/MX/PX is highly demanding as these isomers have overlapping physical properties.<sup>5,6</sup> Chromatographic separation and other processes such as enclathration can be considered as energy saving options however, they are labor and time intensive.<sup>7–10</sup>

Employing porous materials especially for C<sub>8</sub> aromatics separation has recently gained a lot of attention.<sup>11</sup> Zeolites and metal organic frameworks (MOFs) have shown effective industrial separation of OX and PX but more efforts are needed to obtain desired separation performance.<sup>12-17</sup> Porous organic cages, with complementary geometry suitable for specific host molecules, were also employed for energy-demanding separations but showed modest performance for the separation of isomers.18-20 Nonporous adaptive crystals (NACs) based on macrocyclic building blocks such as pillar[6]arene have been successfully utilized for the separation of p-xylene and other isomer from their mixtures in the vapor phase.<sup>4,21,22</sup> Nonetheless, pillar[6]arene crystals can work only via vapor-based adsorption as they are soluble in xylenes, which dramatically limits the possibility for their industrial translation. In this context, our group has recently reported the selective separation of OX and PX by CB[7] and crystalline azo cages, respectively.<sup>6,23</sup> Interestingly, separation of the MX isomer has so far been illusive as host-guest interactions using the molecular sieving approach has mainly preferred PX and OX isomers.

Trianglimine macrocycles have emerged as a novel class of intrinsically porous molecular hosts that can be specifically tailored for selective separations.<sup>24</sup> Herein, we report that macrocycle 1 can be used as a host for the encapsulation and separation of MX from the xylene isomers both in the liquid and vapor phases through shape selective crystallization and the adsorption based approach (Fig. 1a and Fig. S1, ESI†). To the best of our knowledge, no systematic investigation was reported thus far on the use of organic macrocycles for the separation of MX from xylene isomers by the molecular sieving approach.

The synthesis and crystal structure of the macrocyclic host **1** have already been reported by our group.<sup>25,26</sup> It crystallizes in a monoclinic system, chiral space group  $P2_1$  and the asymmetric unit contains one unit of trianglimine and disordered solvent molecules (Table S1, ESI†). The structural analysis also revealed that two trianglimines are nearly perpendicular and stacked in

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental section, adsorption experiments on xylene vapor, <sup>1</sup>H NMR spectra, powder X-ray diffraction patterns, crystallographic information file, thermogravimetric analysis curves, gas chromatograms and DFT calculations. CCDC 2089877, 2089878 and 2091064. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1cc03531b