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1. Materials

All the starting materials including o-bromotoluene (OBT) and m-bromotoluene (MBT) were purchased and used as received. Perbromoethylated pillararenes (BrP5 and BrP6) were synthesized as described previously. S1,S2 Activated BrP5 and BrP6 were prepared according to reported procedures. S3

Table S1. Physical properties of OBT and MBT.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (K)</th>
<th>Boiling Point (K)</th>
<th>Saturated Vapor Pressure at 298 K (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OBT</td>
<td>246.15</td>
<td>453.95</td>
<td>1.2 ± 0.3</td>
</tr>
<tr>
<td>MBT</td>
<td>233.15</td>
<td>455.25</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td>PBT</td>
<td>301.65</td>
<td>456.95</td>
<td>1.0 ± 0.3</td>
</tr>
</tbody>
</table>
2. Methods

2.1. Powder X-Ray Diffraction
X-ray powder diffraction data were measured on a SmartLab diffractometer with fixed divergence slits and a D/tex Ultra 250 detector at room temperature. The diffractometer was configured in parafocusing Bragg-Brentano geometry. Data was collected over a 2-theta range of 5° to 45° with a step size of 0.02° and a scan rate of 5°/min using a Cu $K_a$ radiation at a powder of 40 kV and 180 mA. Cu $K_b$ radiation was removed using a divergent beam Ni filter.

2.2. Thermogravimetric Analysis
TGA was carried out using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. The samples were heated at 10 °C/min using N$_2$ as the protective gas.

2.3. Single Crystal Growth
Single crystals of guest-loaded BrP6 were grown by volatilization: A quantity of 5.00 mg of BrP6 powder in its dried form was carefully dispensed into a small vial where 1.00 mL of the guest was added and the vial was heated until all the powder was dissolved. Colorless crystals were got by volatilization for 2-15 days.

2.4. Single Crystal X-ray Diffraction
Single crystal X-ray diffraction data were collected on a Bruker D8 VENTURE CMOS X-ray diffractometer with graphite monochromatic Mo–$K_a$ radiation ($\lambda = 0.71073$ Å).

2.5. Solution $^1$H NMR Spectroscopy
$^1$H NMR spectra were recorded by using a Bruker Avance DMX 600 spectrometer.

2.6. Gas Chromatography
Gas chromatographic analysis: GC measurements were carried out using an Agilent 7890B instrument configured with an FID detector and a HP-chiralβ column (30 m × 0.32 mm × 0.25 μm). Samples were analyzed using headspace injections and were performed by incubating the sample at 85 °C for 30 min followed by sampling 1.00 mL of the headspace. The total volume of the container is 10 mL; the mass of the solid in the container is about 10 mg; the total volume of the headspace is 1 mL.
3. Crystallographic Data

<table>
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<tbody>
<tr>
<td>Formula</td>
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<td>Crystal System</td>
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<tr>
<td>Space Group</td>
<td>P2₁/c</td>
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<tr>
<td>a [Å]</td>
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</tr>
<tr>
<td>b [Å]</td>
<td>13.7621(10)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>23.8060(17)</td>
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<tr>
<td>α [°]</td>
<td>90</td>
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<tr>
<td>β [°]</td>
<td>90.1300(5)</td>
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<tr>
<td>γ [°]</td>
<td>90</td>
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<tr>
<td>Volume [Å³]</td>
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<tr>
<td>Z</td>
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<tr>
<td>D&lt;sub&gt;calc&lt;/sub&gt; [g cm⁻³]</td>
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<tr>
<td>μ [mm⁻¹]</td>
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<tr>
<td>F(000)</td>
<td>4608.0</td>
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<td>Crystal size [mm³]</td>
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<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>[R&lt;sub&gt;int&lt;/sub&gt; = 0.1427, R&lt;sub&gt;sigma&lt;/sub&gt; = 0.1004]</td>
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</tr>
<tr>
<td>Data/restraints/parameters</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.035</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Final $R$ indexes [$I &gt; 2\sigma (I)$]</td>
<td>$R_1 = 0.1014$, $wR_2 = 0.2582$</td>
</tr>
<tr>
<td>Final $R$ indexes [all data]</td>
<td>$R_1 = 0.1579$, $wR_2 = 0.2943$</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å$^{-3}$</td>
<td>3.01/−1.52</td>
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<tr>
<td>CCDC</td>
<td>2261922</td>
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</table>
4. Characterization of Activated Pillararene Crystals

**Fig. S1** $^1$H NMR spectrum (600 MHz, chloroform-$d$, 298 K) of activated BrP5 crystals.

**Fig. S2** $^1$H NMR spectrum (600 MHz, chloroform-$d$, 298 K) of activated BrP6 crystals.
Fig. S3 Thermogravimetric analysis of activated BrP5 crystals.
Fig. S4 Thermogravimetric analysis of activated BrP6 crystals.
Fig. S5 Powder X-ray diffraction pattern of activated BrP5 crystals.
Fig. S6 Powder X-ray diffraction pattern of activated BrP6 crystals.
5. Vapor-Phase Adsorption Measurements

5.1. Single-Component Monobromotoluene Isomers Adsorption Experiments

Fig. S7 $^1$H NMR spectrum (600 MHz, chloroform-$d$, 298 K) of activated BrP5 crystals after adsorption of OBT vapor. The integration can be calculated as 0.44 equiv. of OBT per BrP5 molecule.

Fig. S8 $^1$H NMR spectrum (600 MHz, chloroform-$d$, 298 K) of activated BrP5 crystals after adsorption of MBT vapor. The integration can be calculated as 1.03 equiv. of MBT per BrP5 molecule.
Fig. S9 Thermogravimetric analysis of activated BrP5 crystals after adsorption of OBT vapor. The weight loss below 100 °C can be calculated as about 0.4 equiv. of OBT per BrP5 molecule.
Fig. S10 Thermogravimetric analysis of activated BrP5 crystals after adsorption of MBT vapor. The weight loss below 100 °C can be calculated as about 1.0 equiv. of MBT per BrP5 molecule.
**Fig. S11** $^1$H NMR spectrum (600 MHz, chloroform-$d$, 298 K) of activated BrP6 crystals after adsorption of OBT vapor. The integration can be calculated as 2.00 equiv. of OBT per BrP6 molecule.

**Fig. S12** $^1$H NMR spectrum (600 MHz, chloroform-$d$, 298 K) of activated BrP6 crystals after adsorption of MBT vapor. The integration can be calculated as 1.28 equiv. of MBT per BrP5 molecule.
Fig. S13 Thermogravimetric analysis of activated BrP6 crystals after adsorption of OBT vapor. The weight loss below 100 °C can be calculated as about 2.0 equiv. of OBT per BrP6 molecule.
Fig. S14 Thermogravimetric analysis of activated BrP6 crystals after adsorption of MBT vapor. The weight loss below 100 °C can be calculated as about 1.2 equiv. of MBT per BrP5 molecule.
5.2. Structural Analyses

Fig. S15 Single crystal structure of (OBT)$_2$@BrP$_6$. [C−H⋯π] distances (Å): 2.70; 2.76; 2.82; 2.82.
Fig. S16 Powder X-ray diffraction patterns of BrP6: (I) after adsorption of OBT vapor; (II) simulated from single crystal structure of (OBT)$_2$@BrP6.
Moreover, we investigated the integration ability of BrP5 with MBT by Job plot and $^1$H NMR titration according to the previous report. The Job plot illustrated that the binding stoichiometry is 1:1 for BrP5 and MBT in CDCl$_3$ (Fig. S17). $^1$H NMR titration experiment demonstrated that the binding constant ($K$) of BrP5 and MBT was 6.01 ± 0.48 M$^{-1}$ (Fig. S18).

**Fig. S17** $^1$H NMR spectra (600 MHz, chloroform-$d$, 298 K): (a) BrP5; (b) BrP5 after adsorbing MBT; (c) MBT. The peaks of MBT displayed upfield shifts in spectrum (b), indicating that MBT was located in the cavity of BrP5 in solution.
Fig. S18 Job plot showing the 1:1 stoichiometry of the complexation between BrP5 and MBT in CDCl₃.
Fig. S19 A plot of the resonance downfield shifts of H₁, H₂ and H₃ of BrP5 versus [MBT] / [BrP5]. The data were fitted to a 1:1 binding model to give $K = 6.01 \pm 0.48 \text{ M}^{-1}$. All solid lines were obtained from non-linear curve-fitting to a 1:1 binding model using the www.supramolecular.org web applet.
5.3. The adsorption behavior of BrP6 to an equal volume MBT and OBT mixture

For each vapor-phase mixture experiment, an open 5.00 mL vial containing 20.00 mg of activated BrP6 adsorbent was placed in a sealed 20.00 mL vial containing 1.00 mL of a 50:50 v/v MBT and OBT mixture. The relative uptake of MBT or OBT by activated BrP6 was measured by heating the crystals to release the adsorbed vapor using gas chromatography. Before measurements, the crystals were heated at 60 °C for half an hour to remove the surface-physically adsorbed vapor.

Fig. S20 ¹H NMR spectrum (600 MHz, chloroform- d, 298 K) of activated BrP6 crystals after adsorption of a 50:50 (v/v) MBT and OBT mixture vapor.
Fig. S21 Time-dependent solid-vapor adsorption plots of BrP6 for MBT and OBT (v:v = 50:50) mixed vapor at 303 K.
Fig. S22 Powder X-ray diffraction patterns of BrP6 crystals: (I) original activated BrP6 crystals; (II) after adsorption of OBT vapor; (III) after adsorption of MBT vapor; (IV) after exposure to MBT and OBT equal volume mixture vapor. The pattern of (IV) resembled the superposition of (II) and (III).
5.4. The adsorption behavior of BrP5 to an equal volume MBT and OBT mixture

For each vapor-phase mixture experiment, an open 5.00 mL vial containing 20.00 mg of activated BrP5 adsorbent was placed in a sealed 20.00 mL vial containing 1.00 mL of a 50:50 v/v MBT and OBT mixture. The relative uptake of MBT or OBT by activated BrP5 was measured by heating the crystals to release the adsorbed vapor using gas chromatography. Before measurements, the crystals were heated at 60 °C for half an hour to remove the surface-physically adsorbed vapor.

Fig. S23 ¹H NMR spectrum (600 MHz, chloroform-d, 298 K) of activated BrP5 crystals after adsorption of a 50:50 v/v MBT and OBT mixture vapor.

Fig. S24 Relative uptake of the MBT/OBT mixture (v:v = 50:50) adsorbed in activated BrP5 crystals after 40 hours.
5.5. *The adsorption behavior of BrP5 to different volume MBT and OBT mixtures*

For each vapor-phase mixture experiment, an open 5.00 mL vial containing 20.00 mg of activated BrP5 adsorbent was placed in a sealed 20.00 mL vial containing 1.00 mL of different volume MBT and OBT mixtures. The volume ratios of MBT and OBT were 20:80, 40:60, 60:40, 80:20, respectively. The relative uptake of MBT or OBT by activated BrP5 was measured by heating the crystals to release the adsorbed vapor using gas chromatography. Before measurements, the crystals were heated at 60 °C for half an hour to remove the surface-physically adsorbed vapor.

**Fig. S25** Relative uptake of the MBT/OBT mixture *(v:v = 20:80)* adsorbed in activated BrP5 crystals after 40 hours.

**Fig. S26** Relative uptake of the MBT/OBT mixture *(v:v = 40:60)* adsorbed in activated BrP5 crystals after 40 hours.
Fig. S27 Relative uptake of the MBT/OBT mixture (v:v = 60:40) adsorbed in activated BrP5 crystals after 40 hours.

Fig. S28 Relative uptake of the MBT/OBT mixture (v:v = 80:20) adsorbed in activated BrP5 crystals after 40 hours.
6. Recyclability Test

Recyclability of Activated BrP5 Crystals

An open 5.00 mL vial containing 20.00 mg of BrP5 after adsorption was desolvated under vacuum at 100 °C overnight. The resultant crystals were characterized by PXRD and 1H NMR.

![Powder X-ray diffraction patterns of BrP5 crystals](image)

**Fig. S29** Powder X-ray diffraction patterns of BrP5 crystals: (I) original activated BrP5 crystals; (II) BrP5 crystals after exposure to MBT and OBT equal volume mixture vapor; (III) desolvated BrP5 crystals.
Fig. S30 $^1$H NMR spectra (600 MHz, chloroform-$d$, 298 K): (a) original activated BrP5 crystals; (b) BrP5 crystals after exposure to MBT and OBT equal volume mixture vapor; (c) desolvated BrP5 crystals.

Fig. S31 The first cycle of adsorption of the equal volume mixture of MBT and OBT by BrP5 crystals measured by GC.
Fig. S32 The second cycle of adsorption of the equal volume mixture of MBT and OBT by BrP5 crystals measured by GC.

Fig. S33 The third cycle of adsorption of the equal volume mixture of MBT and OBT by BrP5 crystals measured by GC.
Fig. S34 The fourth cycle of adsorption of the equal volume mixture of MBT and OBT by BrP5 crystals measured by GC.

Fig. S35 The fifth cycle of adsorption of the equal volume mixture of MBT and OBT by BrP5 crystals measured by GC.
7. References


