Efficient Separation of Monobromotoluene Isomers by Nonporous Adaptive Perbromoethylated Pillar[5]arene Crystals

Bohan Zhao,[#a] Jianwei Wang,[#a,b] Li Shao,[d] Yitao Wu,[a] Ming Li,[a] Bin Hua*[a,b] and Feihe Huang*[a,b,c]*

[a] *Stoddart Institute of Molecular Science, Department of Chemistry, Zhejiang University, Hangzhou 310058, P. R. China; Fax and Tel: +86-571-8795-3189. Email addresses: mingzhelee@zju.edu.cn; huabin@zju.edu.cn; fhuang@zju.edu.cn*

[b] *Zhejiang-Israel Joint Laboratory of Self-Assembling Functional Materials, ZJU-Hangzhou Global Scientific and Technological Innovation Center, Zhejiang University, Hangzhou 311215, P. R. China*

[c] *Green Catalysis Center and College of Chemistry, Zhengzhou University, Zhengzhou 450001, P. R. China*

[d] *Department of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China*

Electronic Supplementary Information (33 pages)

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**.

Compound	Melting Point (K)	Boiling Point (K)	Saturated Vapor Pressure at 298 K (mm Hg)
OBT	246.15	453.95	1.2 ± 0.3
MBT	233.15	455.25	1.1 ± 0.3
PBT	301.65	456.95	1.0 ± 0.3

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_α radiation at a powder of 40 kV and 180 mA. Cu K_β 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_α radiation (λ = 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 S2. Experimental single crystal X-ray data for (**OBT**)$_2$@**BrP6**.

Collection Temperature [K]	170.00
Formula	$C_{80}H_{86}Br_{14}O_{12}$
Crystal System	monoclinic
Space Group	$P2_1/c$
a [Å]	25.7704(16)
b [Å]	13.7621(10)
c [Å]	23.8060(17)
α [°]	90
β [°]	90.1300(5)
γ [°]	90
Volume [Å^3]	8442.9(10)
Z	4
D_{calcd} [g cm^{-3}]	1.855
μ [mm^{-1}]	6.697
F(000)	4608.0
Crystal size [mm^3]	0.23 × 0.13 × 0.06
Radiation	Mo$K\alpha$ (λ = 0.71073)
2θ range [°]	3.77 to 55.123
Index ranges	$-33 \le h \le 33$, $-17 \le k \le 17$, $-30 \le l \le 30$
Reflections collected	128129
Independent reflections	19153 [R_{int} = 0.1427, R_{sigma} = 0.1004]
Data/restraints/parameters	19153/1066/1152

Goodness-of-fit on F^2	1.035
Final R indexes [$I>2\sigma(I)$]	$R_1 = 0.1014$, $wR_2 = 0.2582$
Final R indexes [all data]	$R_1 = 0.1579$, $wR_2 = 0.2943$
Largest diff. peak/hole / e Å^{-3}	3.01/−1.52
CCDC	2261922

4. Characterization of Activated Pillararene Crystals

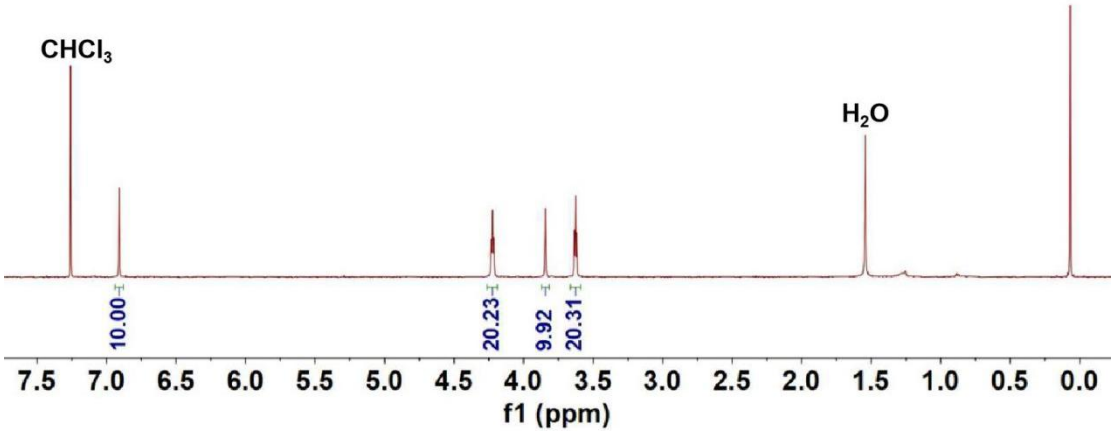

Fig. S1 ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of activated **BrP5** crystals.

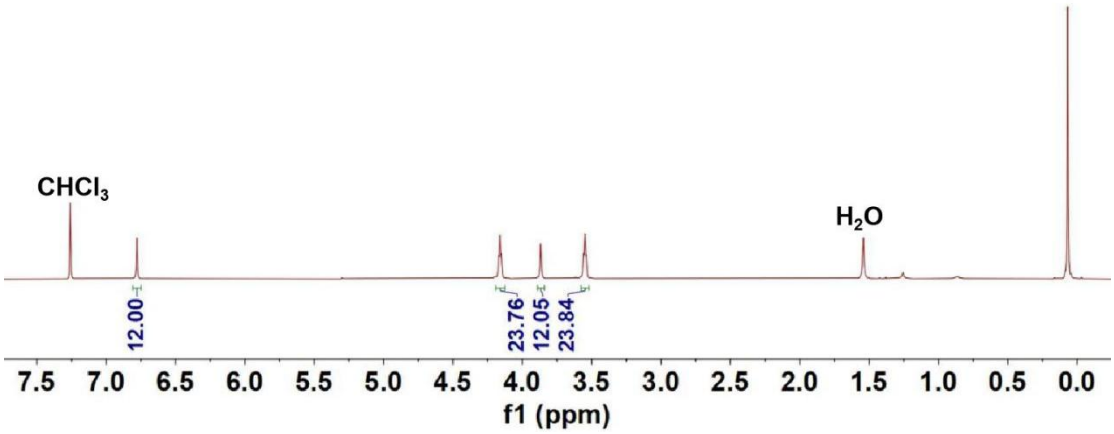

Fig. S2 ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of activated **BrP6** crystals.

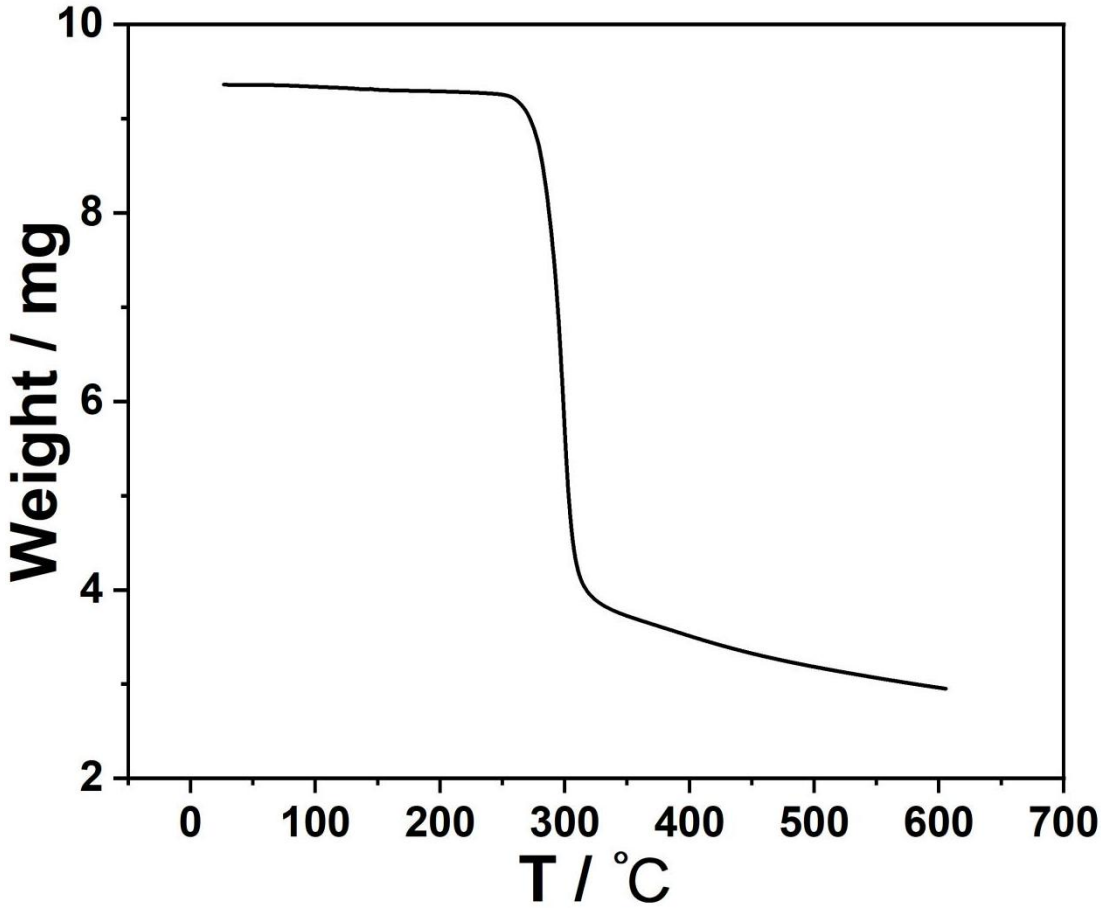

Fig. S3 Thermogravimetric analysis of activated **BrP5** crystals.

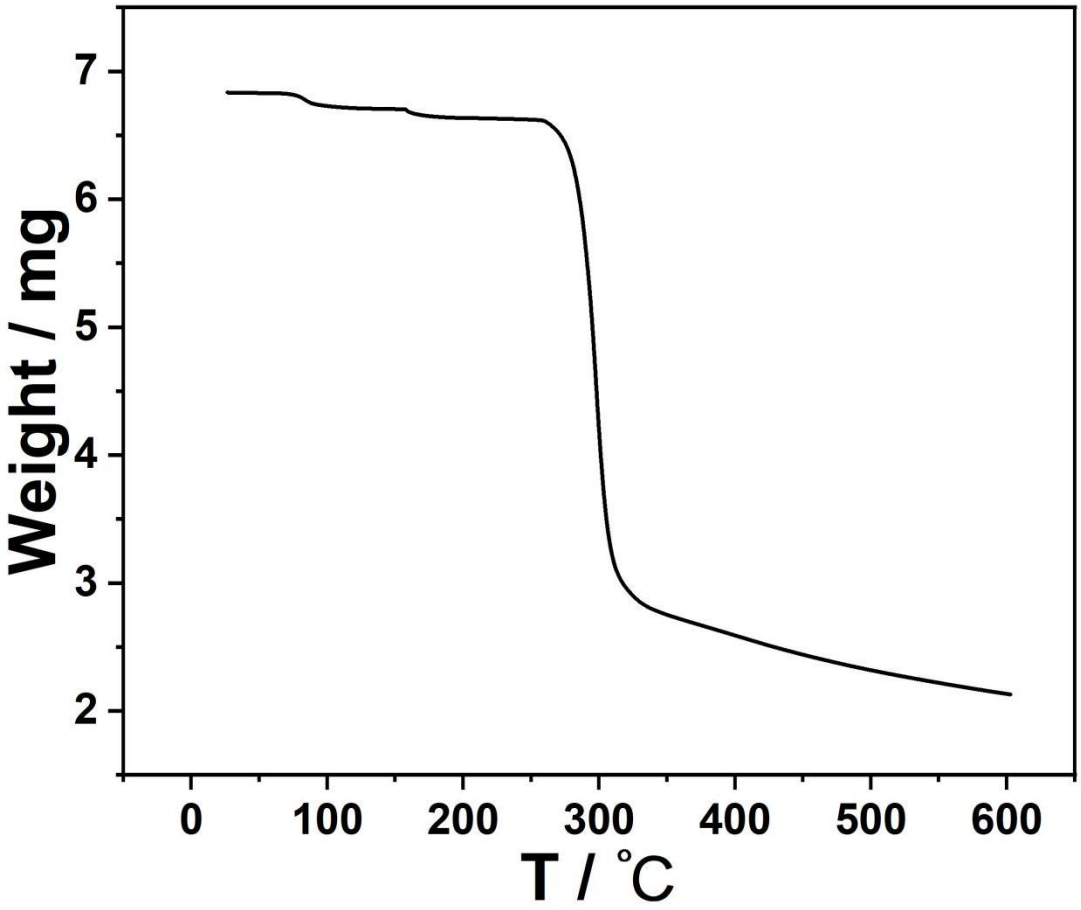

Fig. S4 Thermogravimetric analysis of activated **BrP6** crystals.

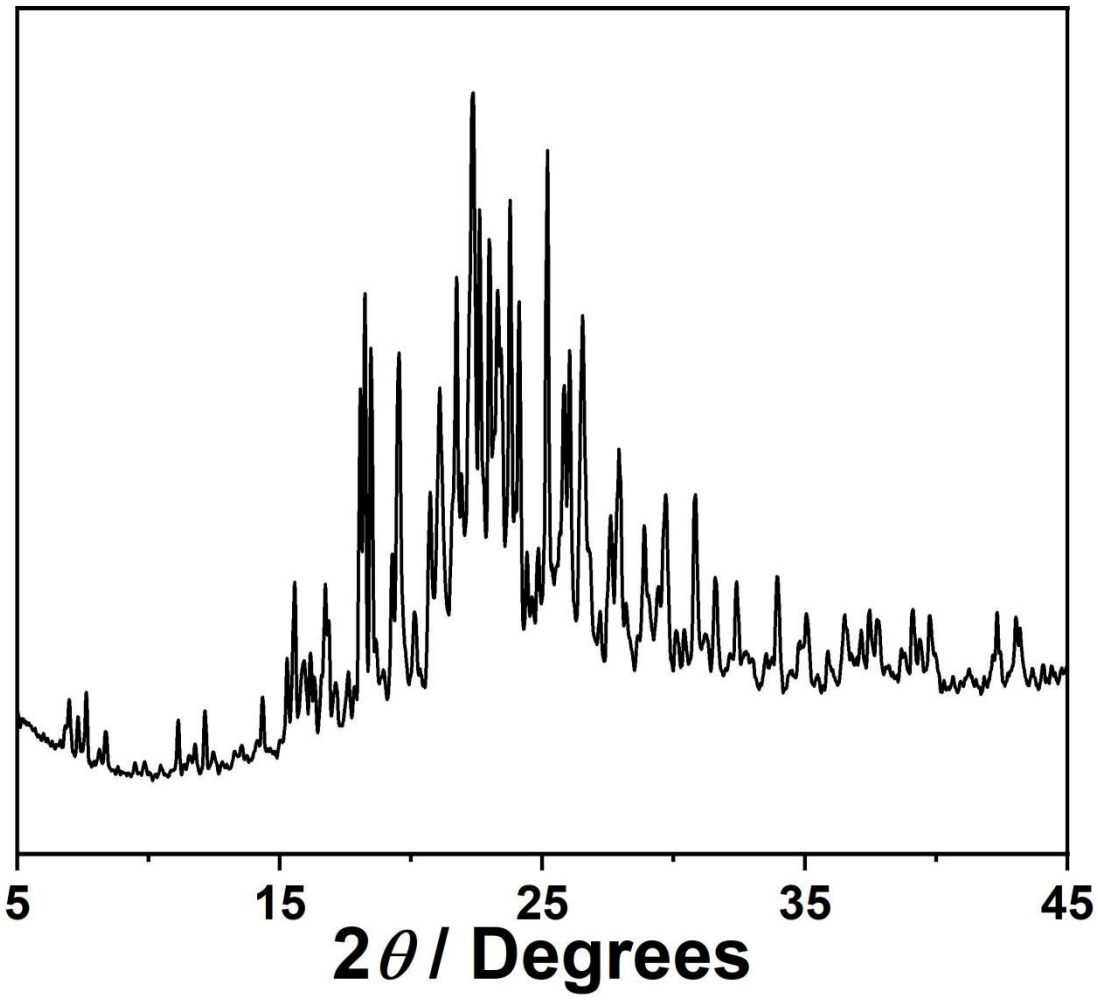

Fig. S5 Powder X-ray diffraction pattern of activated **BrP5** crystals.

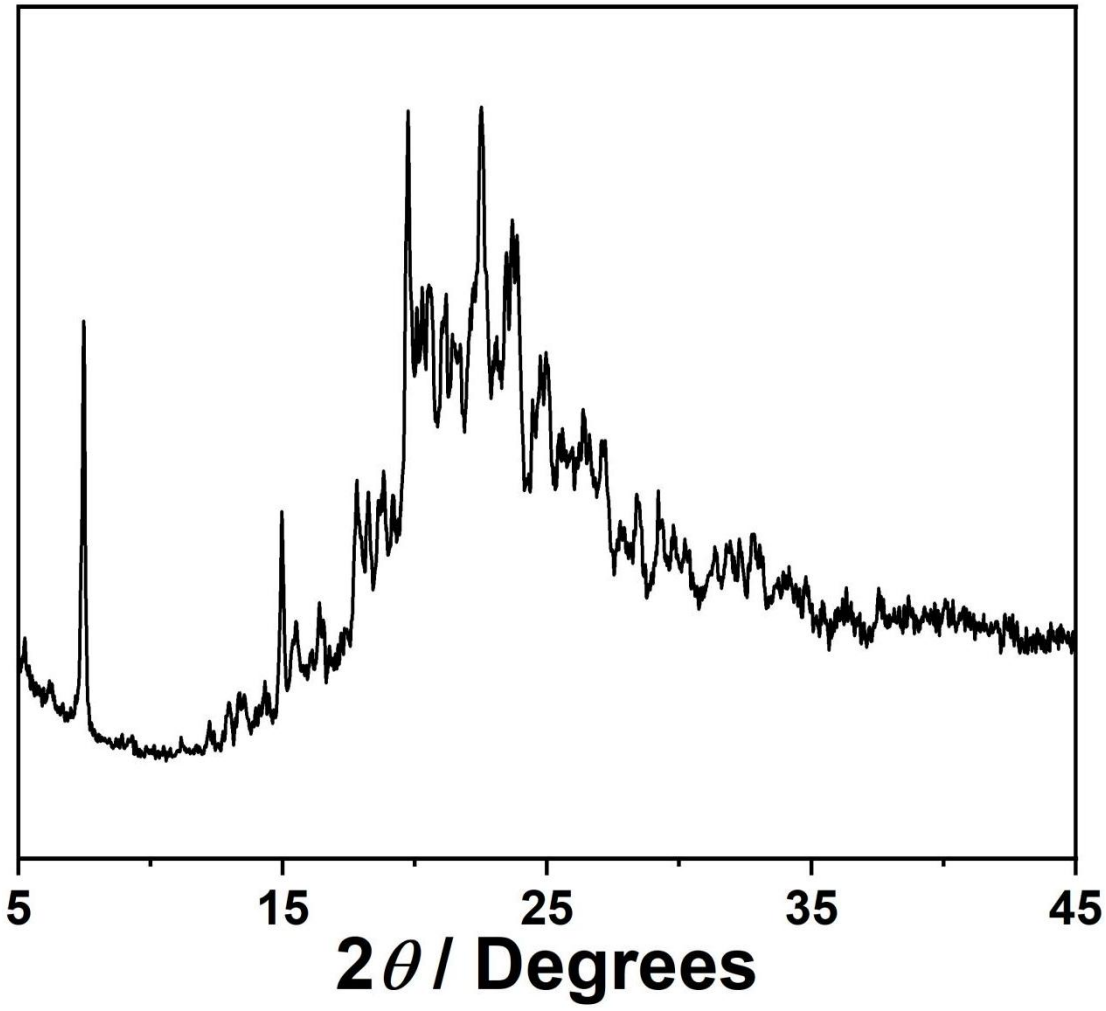

Fig. S6 Powder X-ray diffraction pattern of activated **BrP6** crystals.

5. Vapor-Phase Adsorption Measurements

5.1. Single-Component Monobromotoluene Isomers Adsorption Experiments

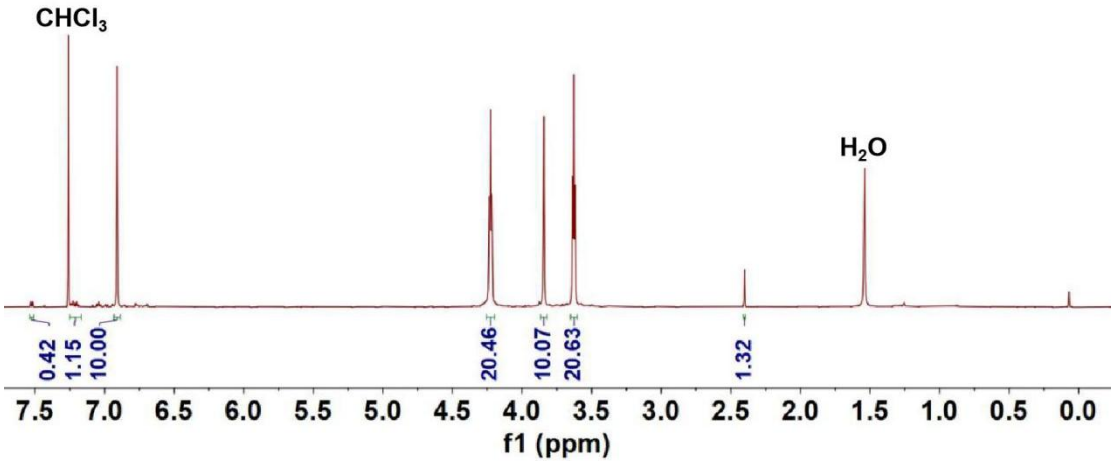

Fig. S7 ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of activated **BrP5** crystals after adsorption of **OBT** vapor. The integration can be calculated as 0.44 equiv. of **OBT** per **BrP5** molecule.

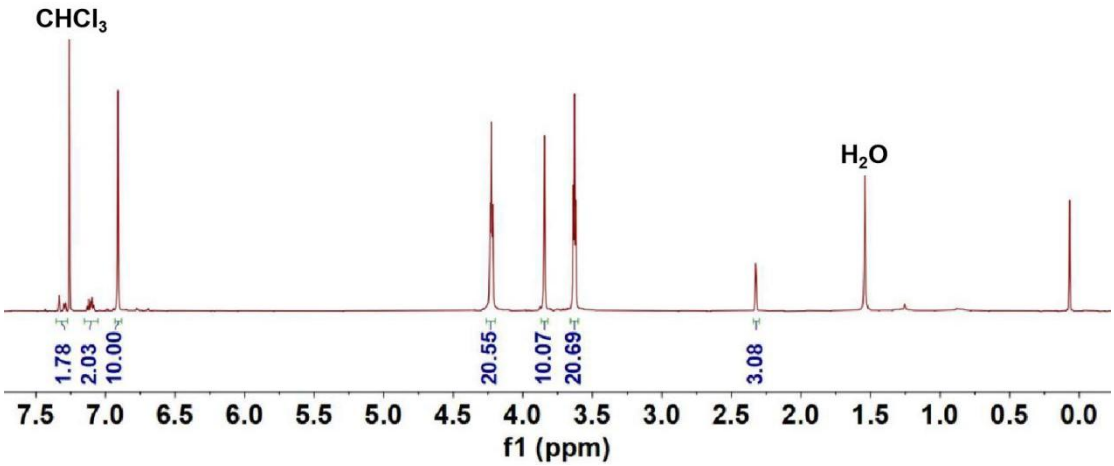

Fig. S8 ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of activated **BrP5** crystals after adsorption of **MBT** vapor. The integration can be calculated as 1.03 equiv. of **MBT** per **BrP5** molecule.

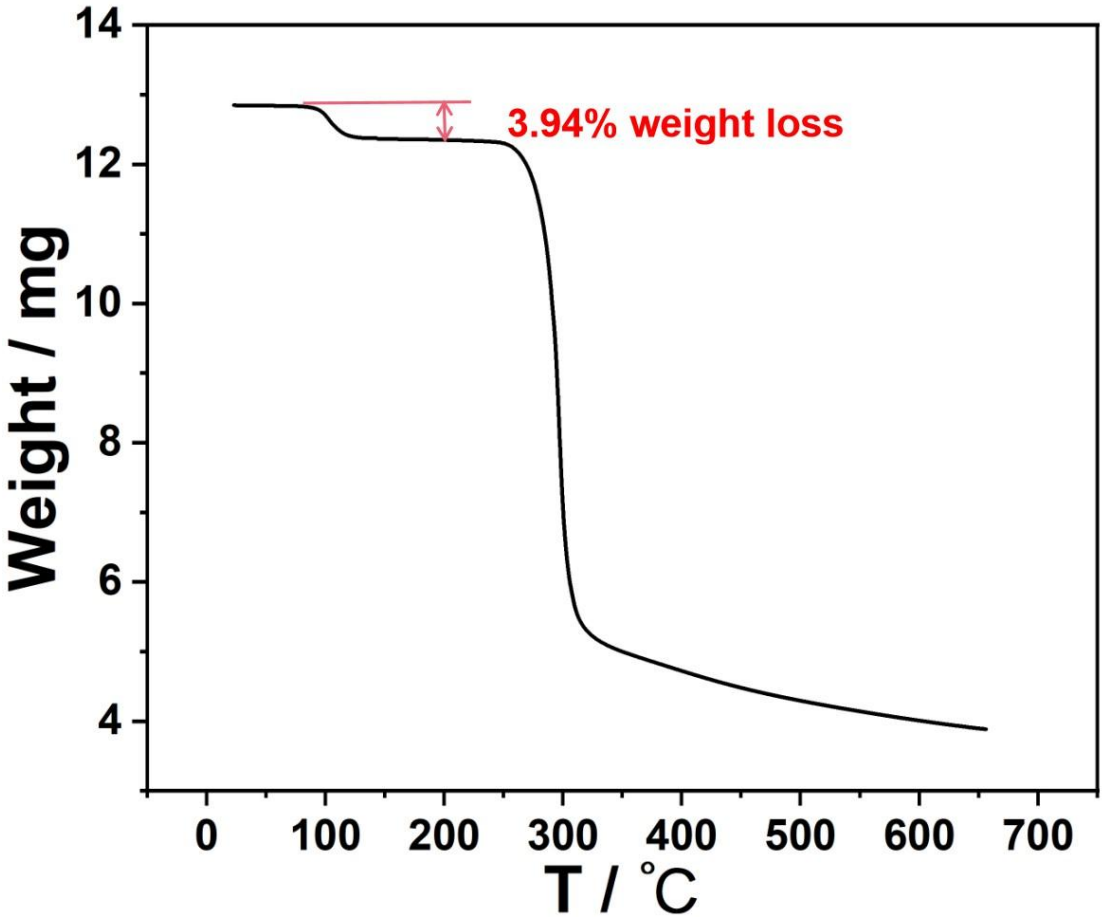

Fig. S9 Thermogravimetric analysis of activated **BrP5** crystals after adsorption of **OBT** vapor. The weight loss below 100 ℃ can be calculated as about 0.4 equiv. of **OBT** per **BrP5** molecule.

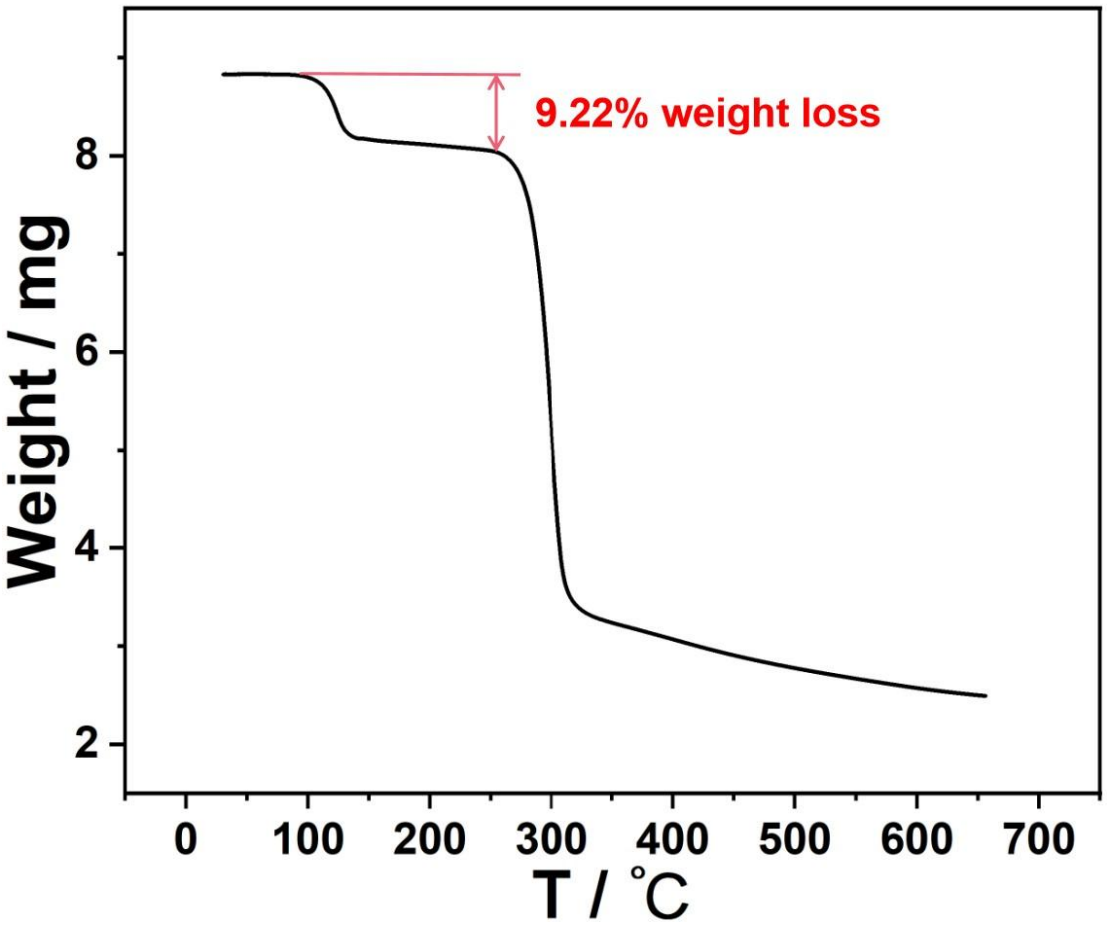

Fig. S10 Thermogravimetric analysis of activated **BrP5** crystals after adsorption of **MBT** vapor. The weight loss below 100 ℃ can be calculated as about 1.0 equiv. of **MBT** per **BrP5** molecule.

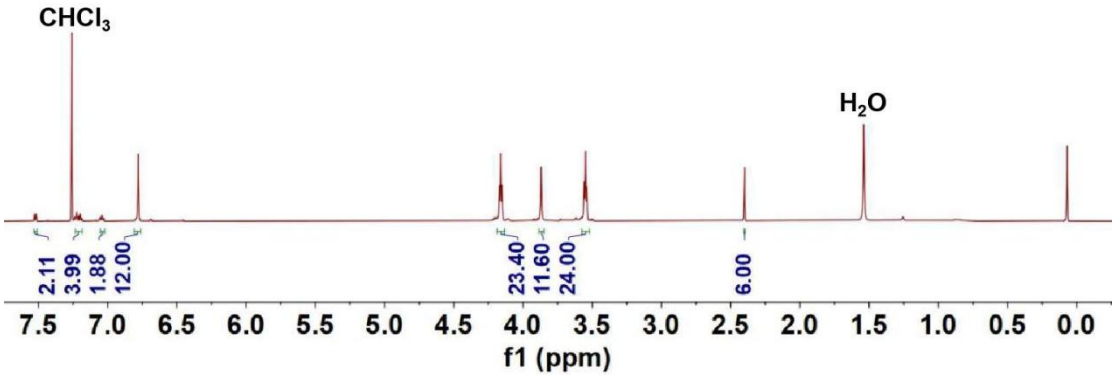

Fig. S11 ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of activated **BrP6** crystals after adsorption of **OBT** vapor. The integration can be calculated as 2.00 equiv. of **OBT** per **BrP6** molecule.

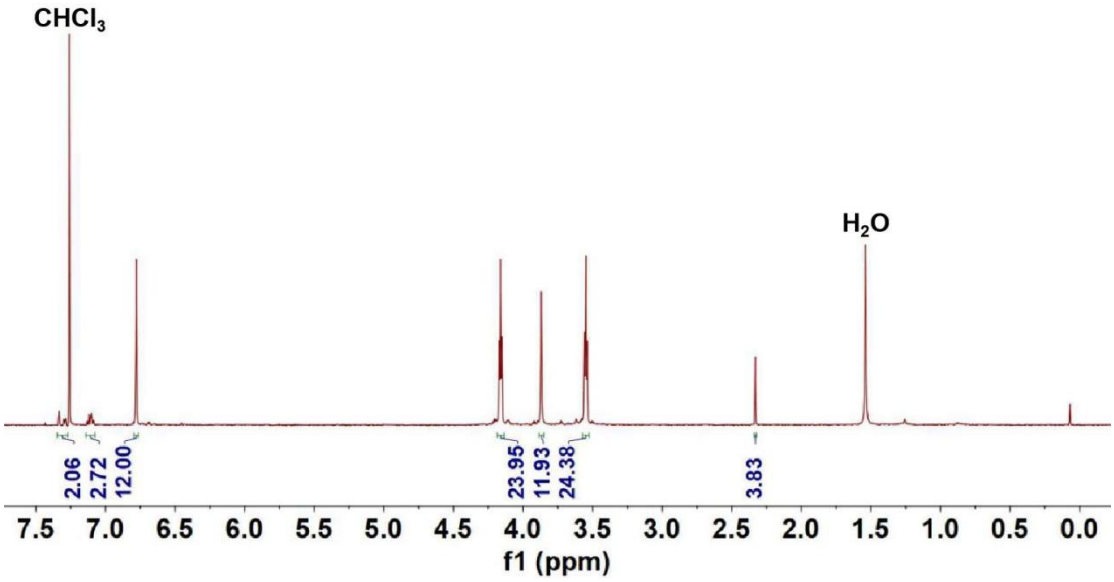

Fig. S12 ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of activated **BrP6** crystals after adsorption of **MBT** vapor. The integration can be calculated as 1.28 equiv. of **MBT** per **BrP5** molecule.

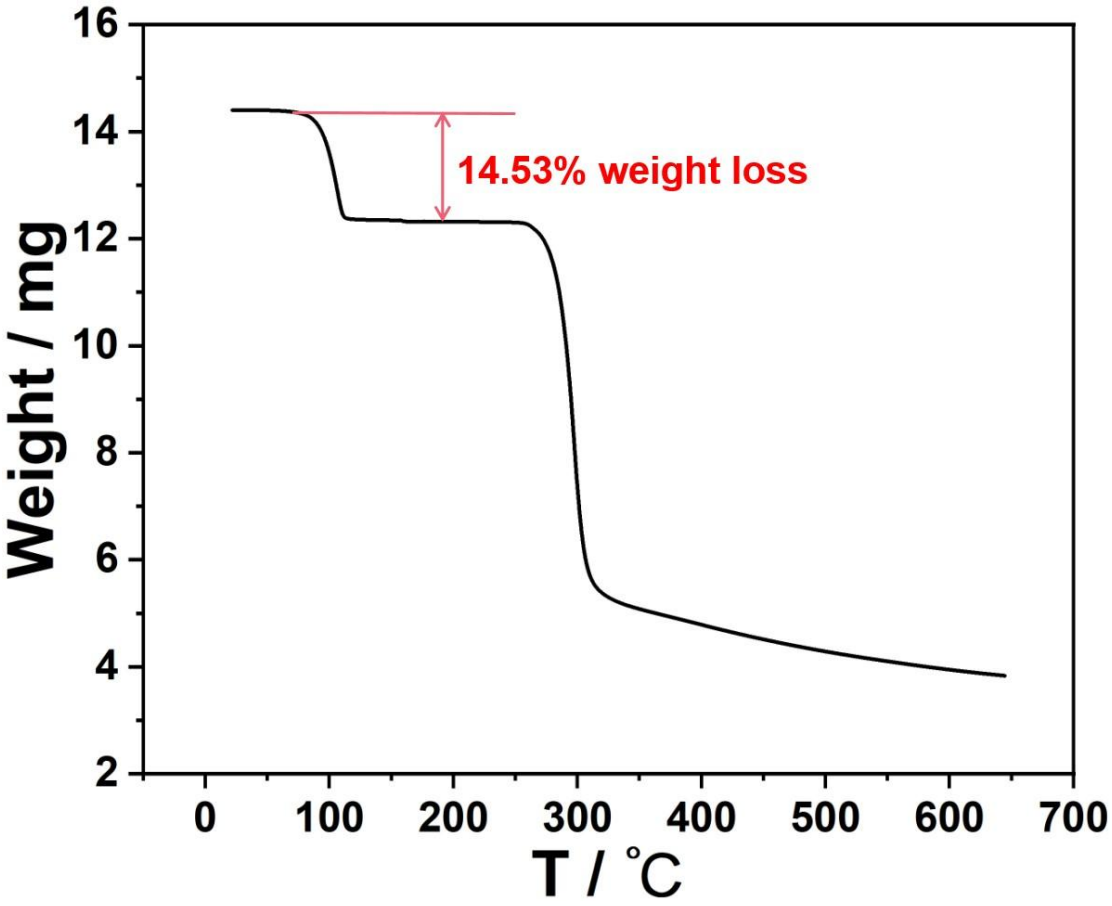

Fig. S13 Thermogravimetric analysis of activated **BrP6** crystals after adsorption of **OBT** vapor. The weight loss below 100 ℃ can be calculated as about 2.0 equiv. of **OBT** per **BrP6** molecule.

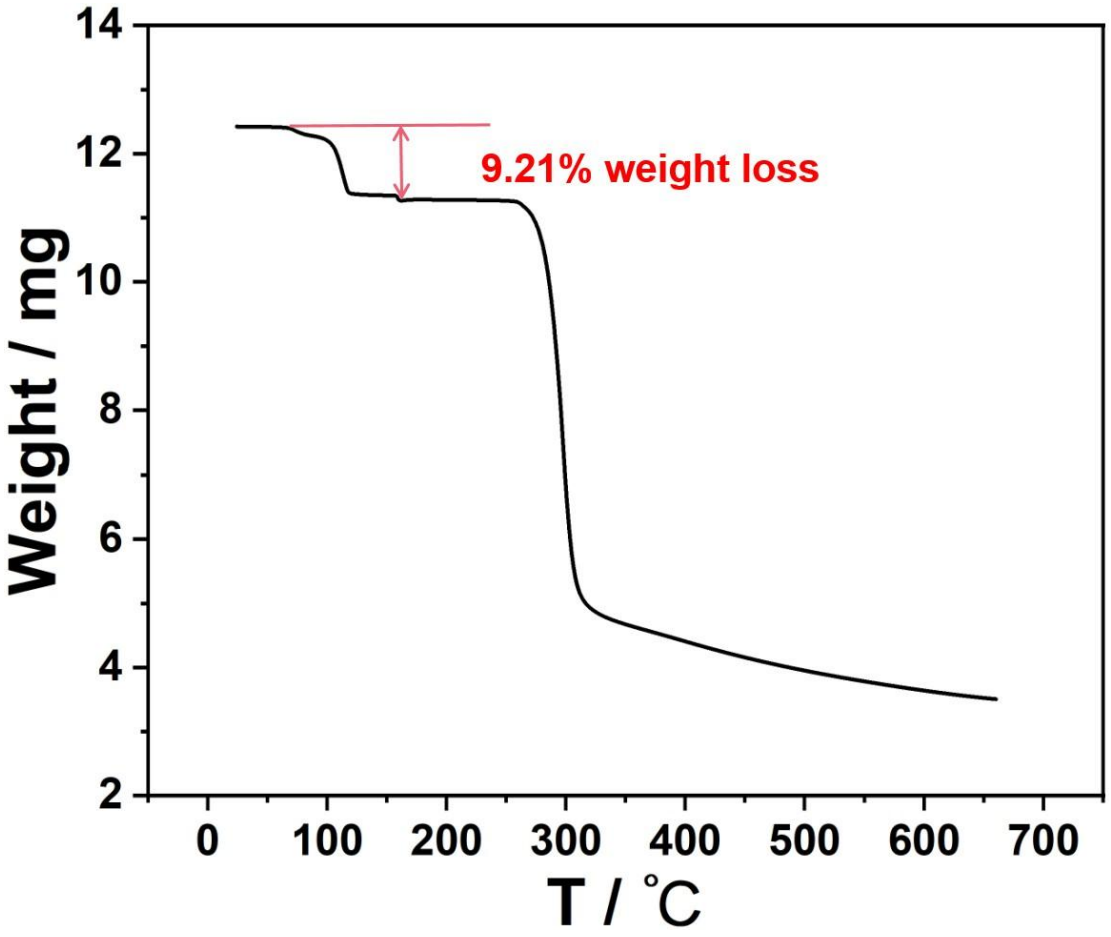

Fig. S14 Thermogravimetric analysis of activated **BrP6** crystals after adsorption of **MBT** vapor. The weight loss below 100 ℃ can be calculated as about 1.2 equiv. of **MBT** per **BrP5** molecule.

5.2. Structural Analyses

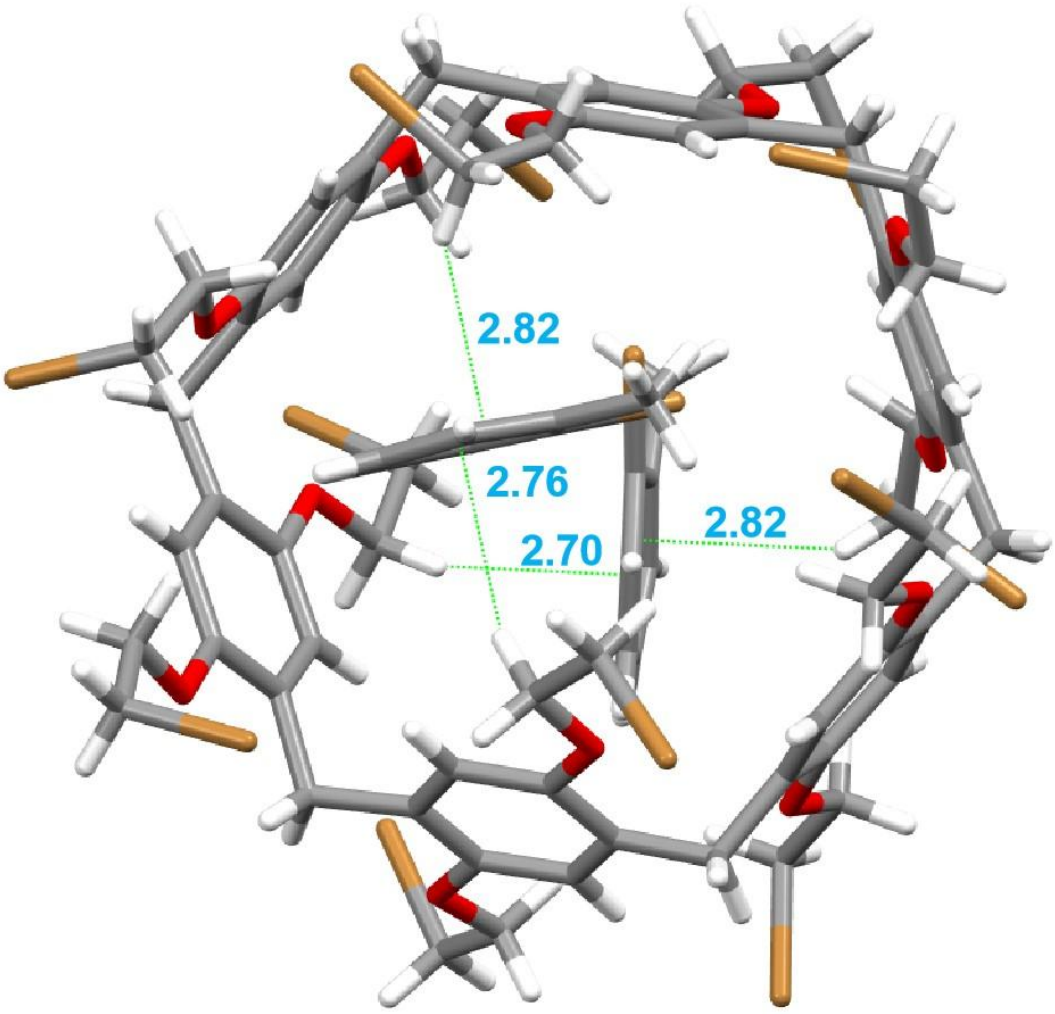

Fig. S15 Single crystal structure of (**OBT**)$_2$@**BrP6**. [C−H···π] distances (Å): 2.70；2.76；2.82；2.82.

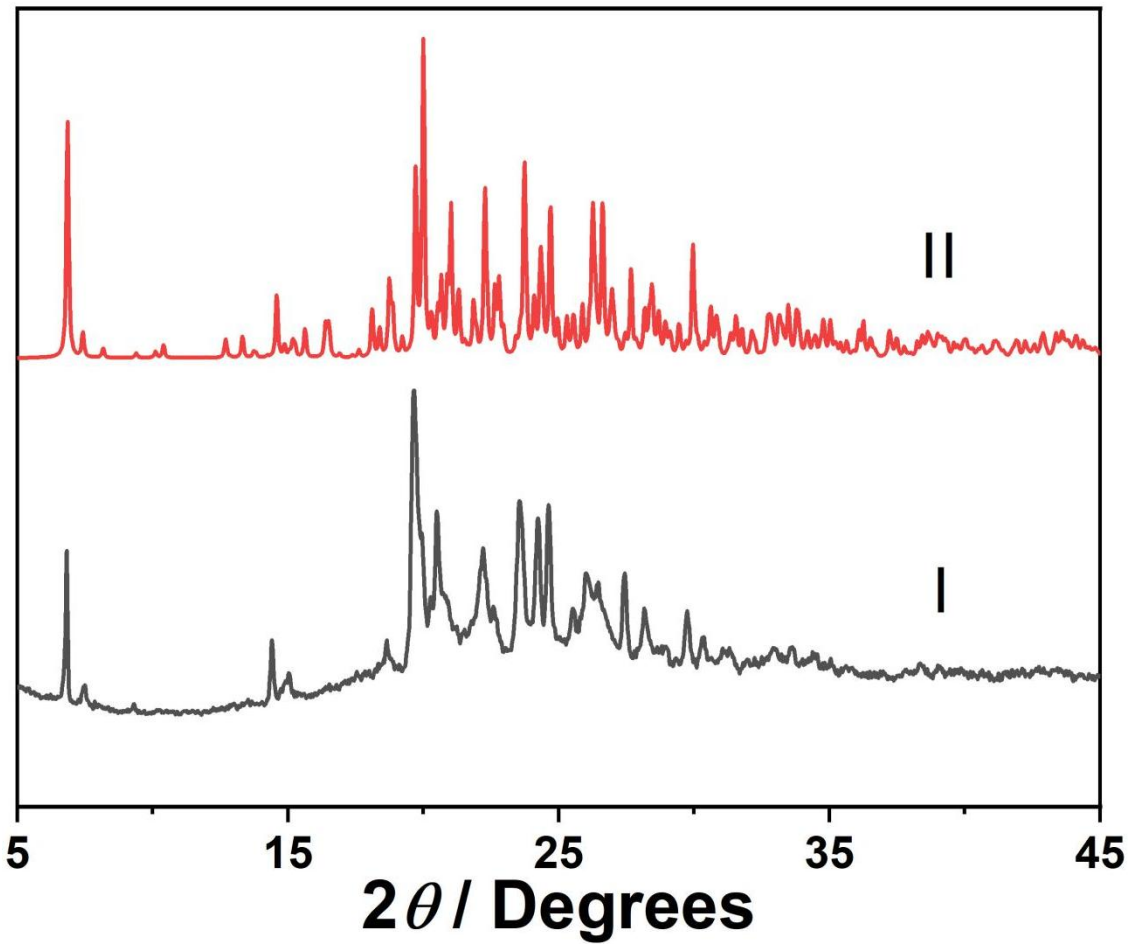

Fig. S16 Powder X-ray diffraction patterns of **BrP6**: (I) after adsorption of **OBT** vapor; (II) simulated from single crystal structure of (**OBT**)$_2$@**BrP6**.

Moreover, we investigated the integration ability of **BrP5** with **MBT** by Job plot and ^{1}H NMR titration according to the previous report.[S4] 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).

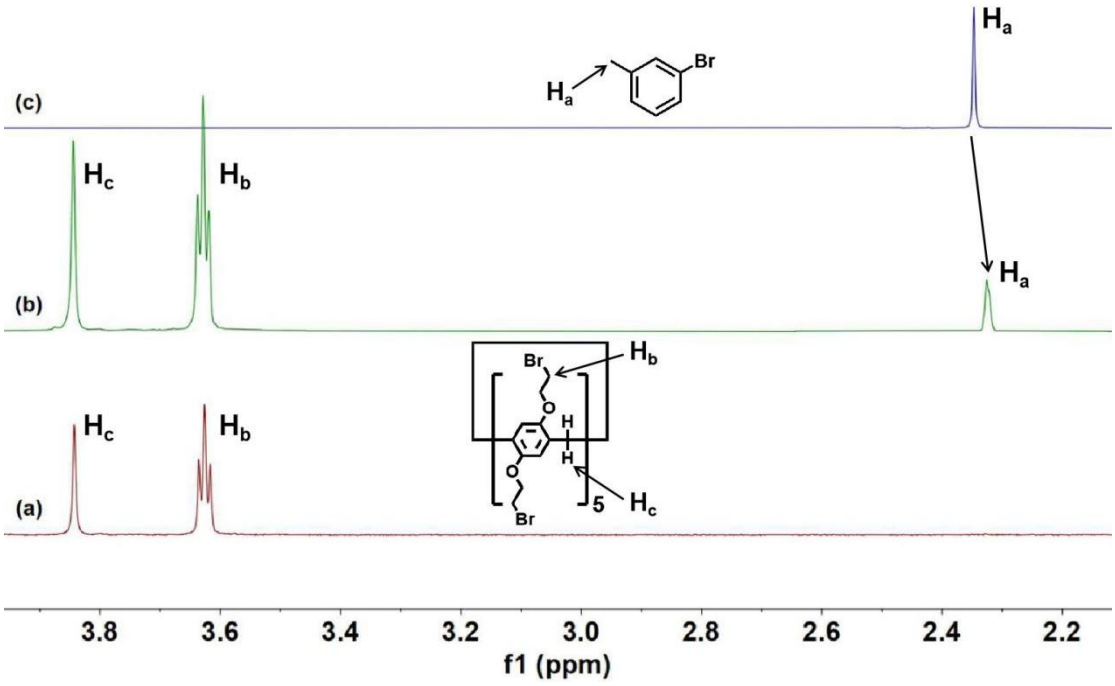

Fig. S17 ^{1}H NMR spectra (600 MHz, chloroform-*d*, 298 K): (a) **BrP5**; (b) **BrP5** after adsorbing **MBT**; (c) **MBT**. The peaks of **MBT** displayed upfield shifts in spectrum (b), indicating that **MBT** was located in the cavity of **BrP5** in solution.

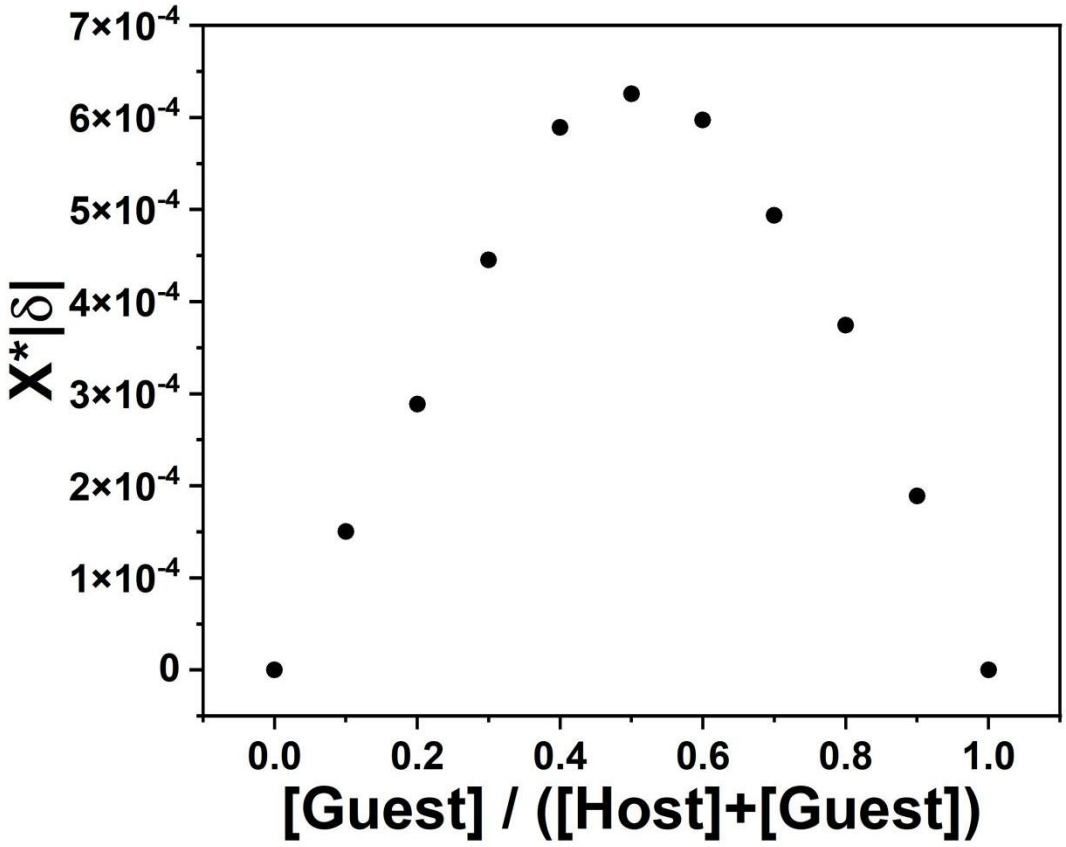

Fig. S18 Job plot showing the 1:1 stoichiometry of the complexation between **BrP5** and **MBT** in $CDCl_3$.

Fig. S19 A plot of the resonance downfield shifts of H_1, H_2 and H_3 of **BrP5** versus [**MBT**] / [**BrP5**]. The data were fitted to a 1:1 binding model to give K = 6.01 ± 0.48 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 ℃ for half an hour to remove the surface-physically adsorbed vapor.

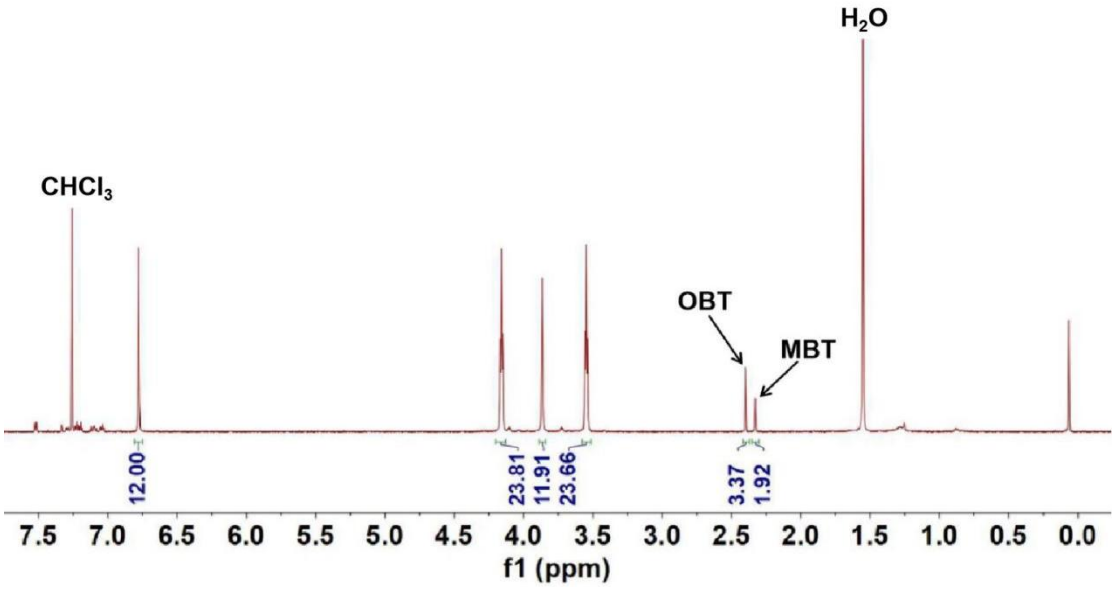

Fig. S20 ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of activated **BrP6** crystals after adsorption of a 50:50 (*v*/*v*) **MBT** and **OBT** mixture vapor.

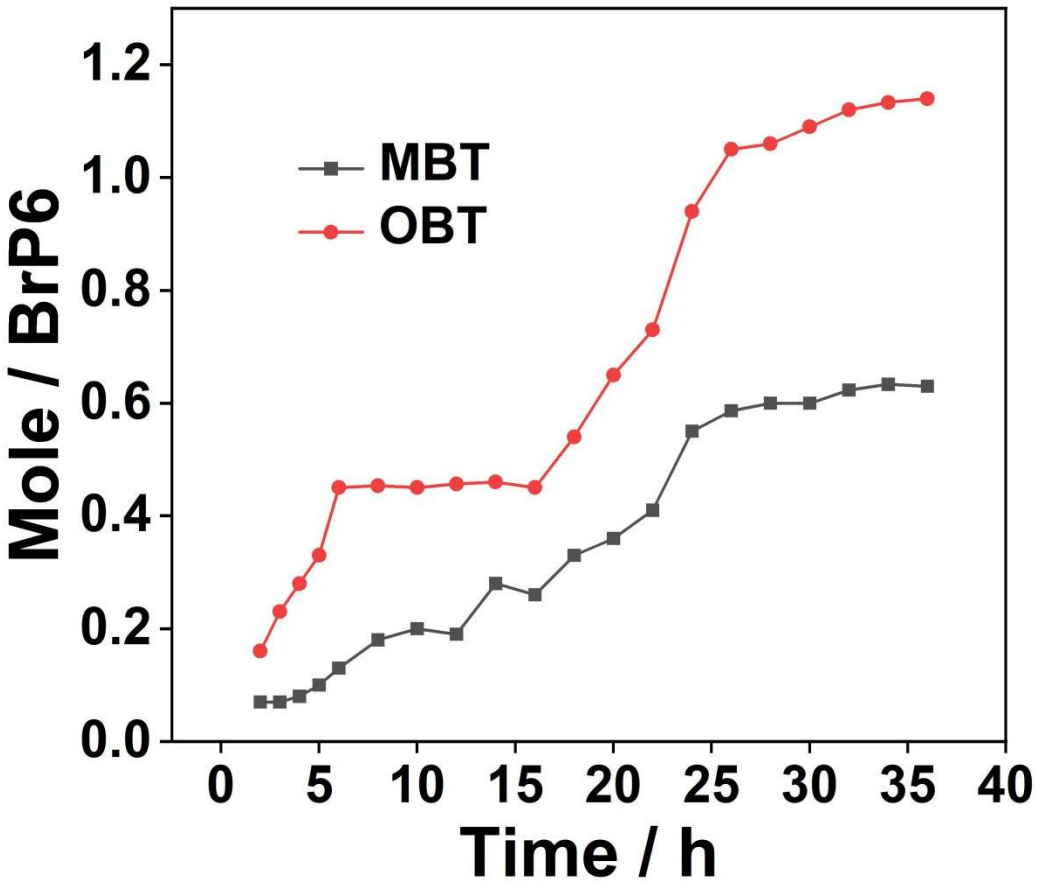

Fig. S21 Time-dependent solid-vapor adsorption plots of **BrP6** for **MBT** and **OBT** (*v*:*v* = 50:50) mixed vapor at 303 K.

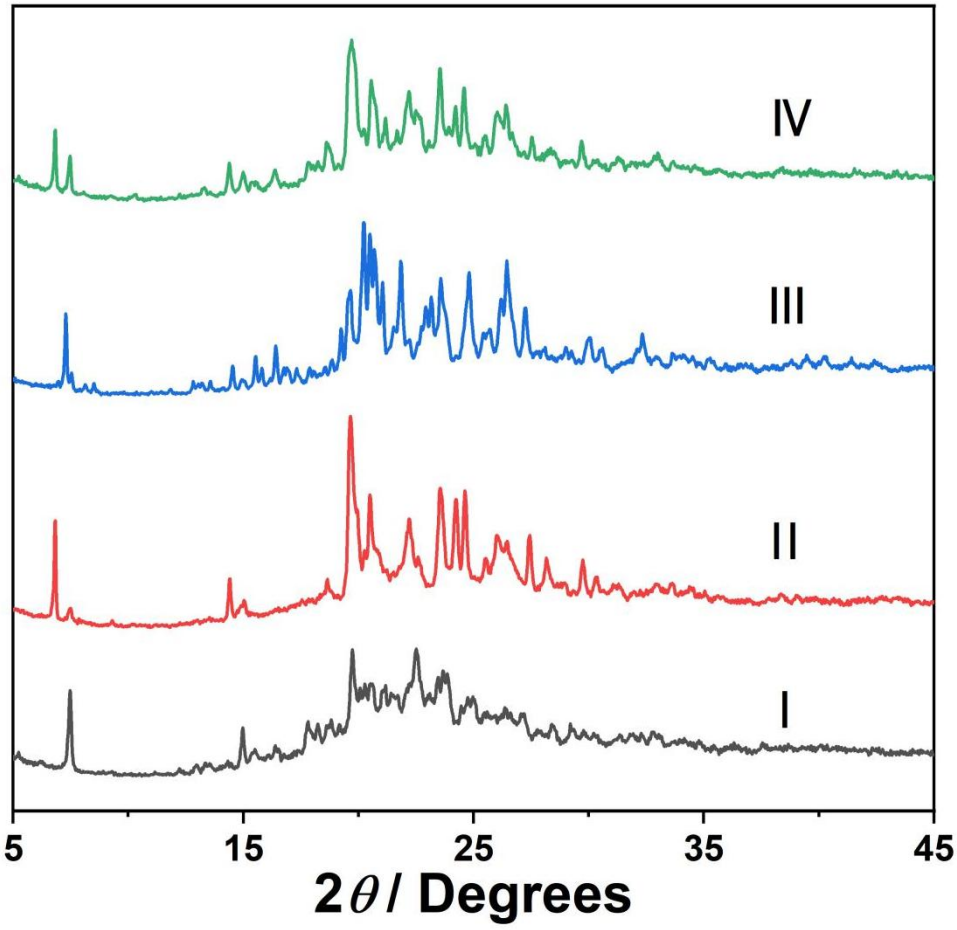

Fig. S22 Powder X-ray diffraction patterns of **BrP6** crystals: (I) original activated **BrP6** crystals; (II) after adsorption of **OBT** vapor; (III) after adsorption of **MBT** vapor; (IV) after exposure to **MBT** and **OBT** equal volume mixture vapor. The pattern of (IV) resembled the superposition 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 ℃ for half an hour to remove the surface-physically adsorbed vapor.

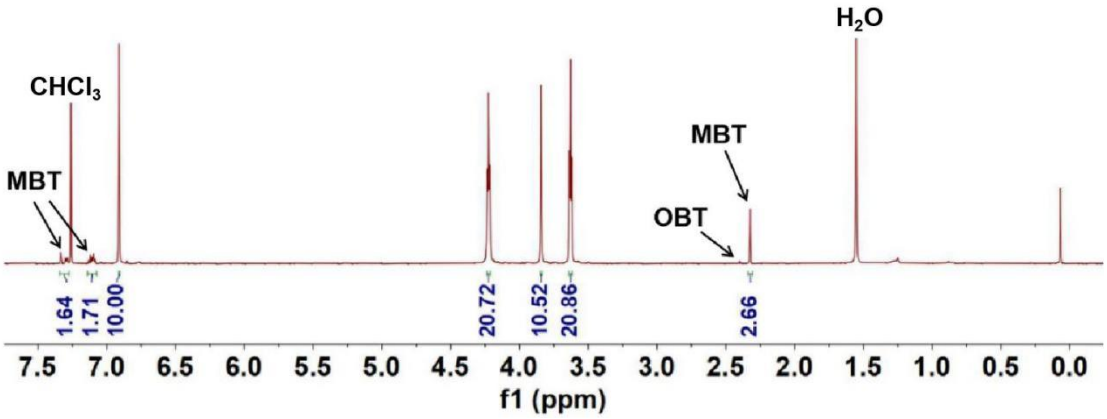

Fig. S23 ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of activated **BrP5** crystals after adsorption of a 50:50 *v*/*v* **MBT** and **OBT** mixture vapor.

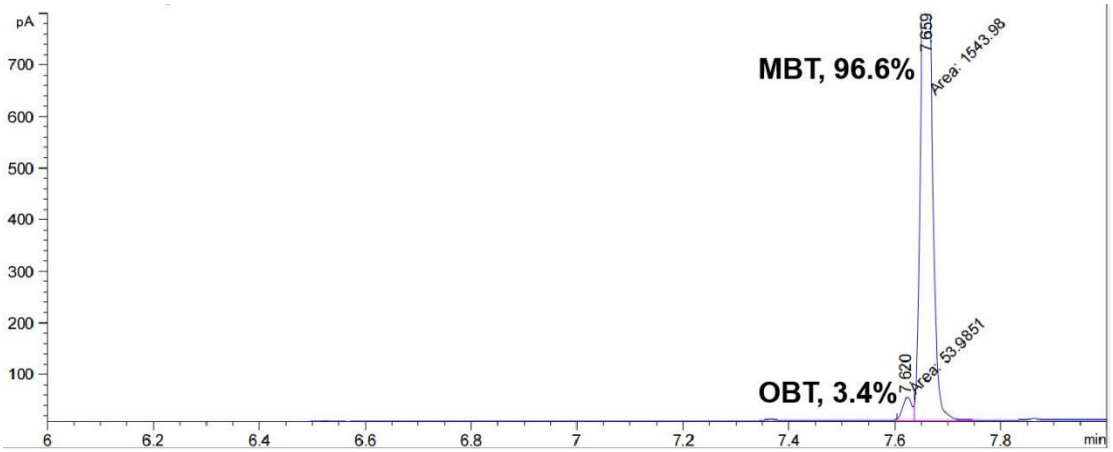

Fig. S24 Relative uptake of the **MBT**/**OBT** mixture (*v*:*v* = 50:50) adsorbed in activated **BrP5** crystals after 40 hours.

*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 ℃ for half an hour to remove the surface-physically adsorbed vapor.

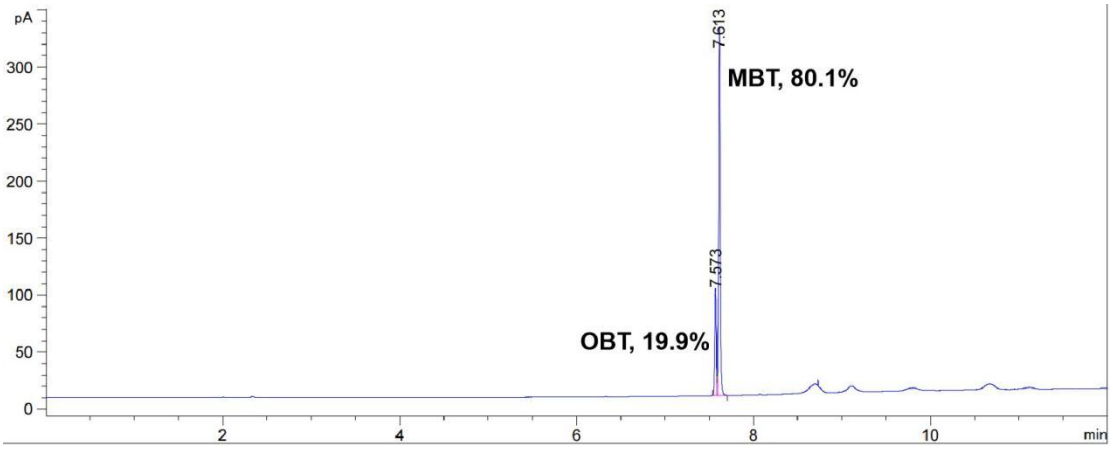

Fig. S25 Relative uptake of the **MBT**/**OBT** mixture (*v:v* = 20:80) adsorbed in activated **BrP5** crystals after 40 hours.

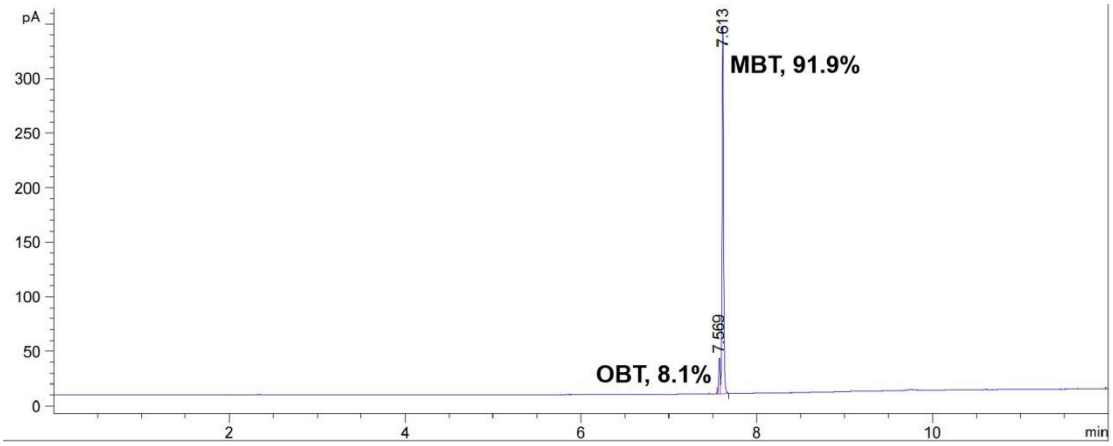

Fig. S26 Relative uptake of the **MBT**/**OBT** mixture (*v:v* = 40:60) adsorbed in activated **BrP5** crystals after 40 hours.

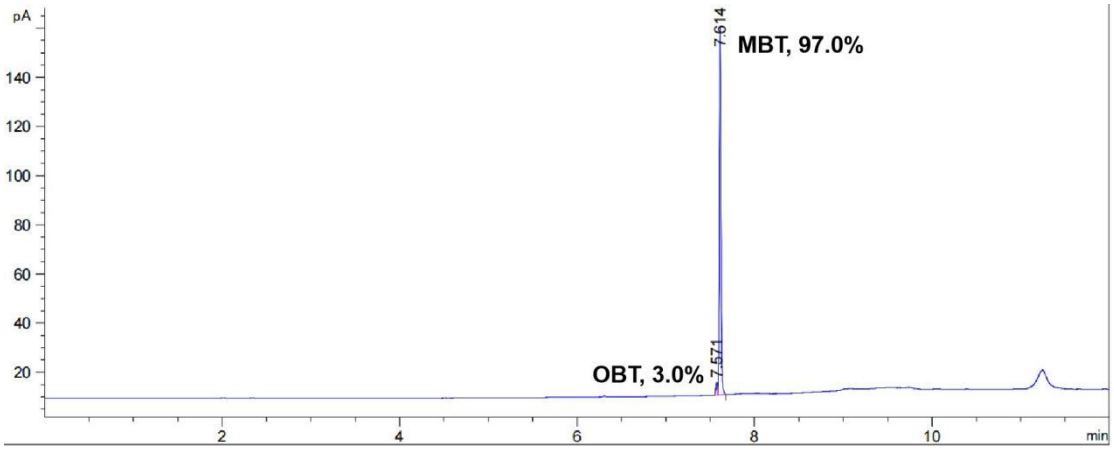

Fig. S27 Relative uptake of the **MBT**/**OBT** mixture (*v*:*v* = 60:40) adsorbed in activated **BrP5** crystals after 40 hours.

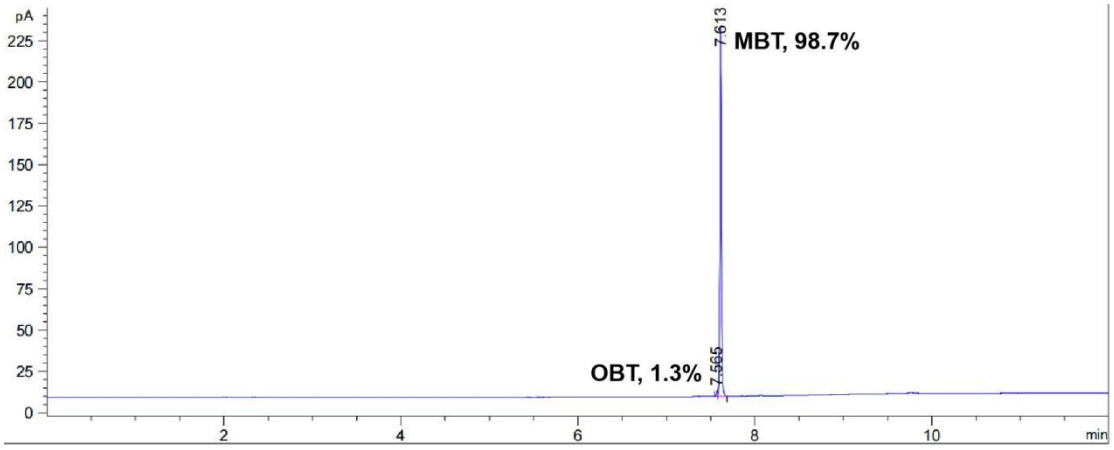

Fig. S28 Relative uptake of the **MBT**/**OBT** mixture (*v*:*v* = 80:20) adsorbed in activated **BrP5** crystals after 40 hours.

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 ℃ overnight. The resultant crystals were characterized by PXRD and ^{1}H NMR.

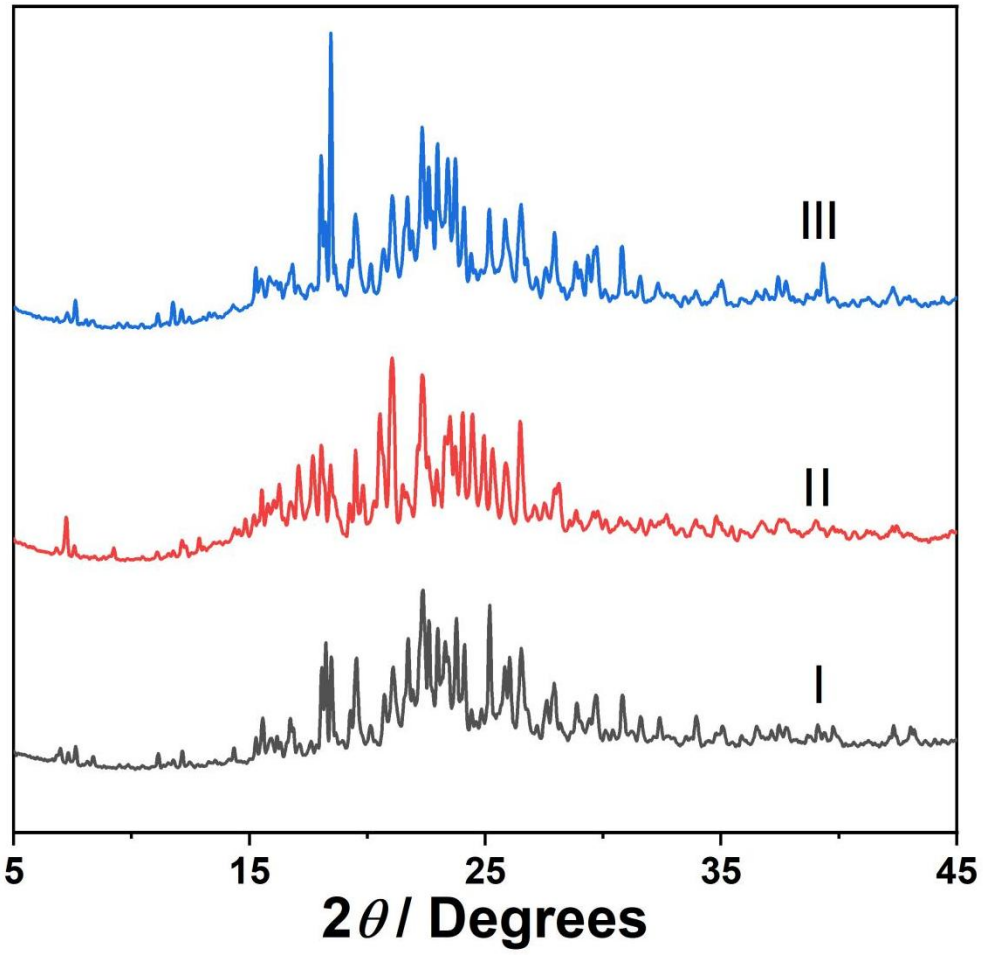

Fig. S29 Powder X-ray diffraction patterns of **BrP5** crystals: (I) original activated **BrP5** crystals; (II) **BrP5** crystals after exposure to **MBT** and **OBT** equal volume mixture vapor; (III) desolvated **BrP5** crystals.

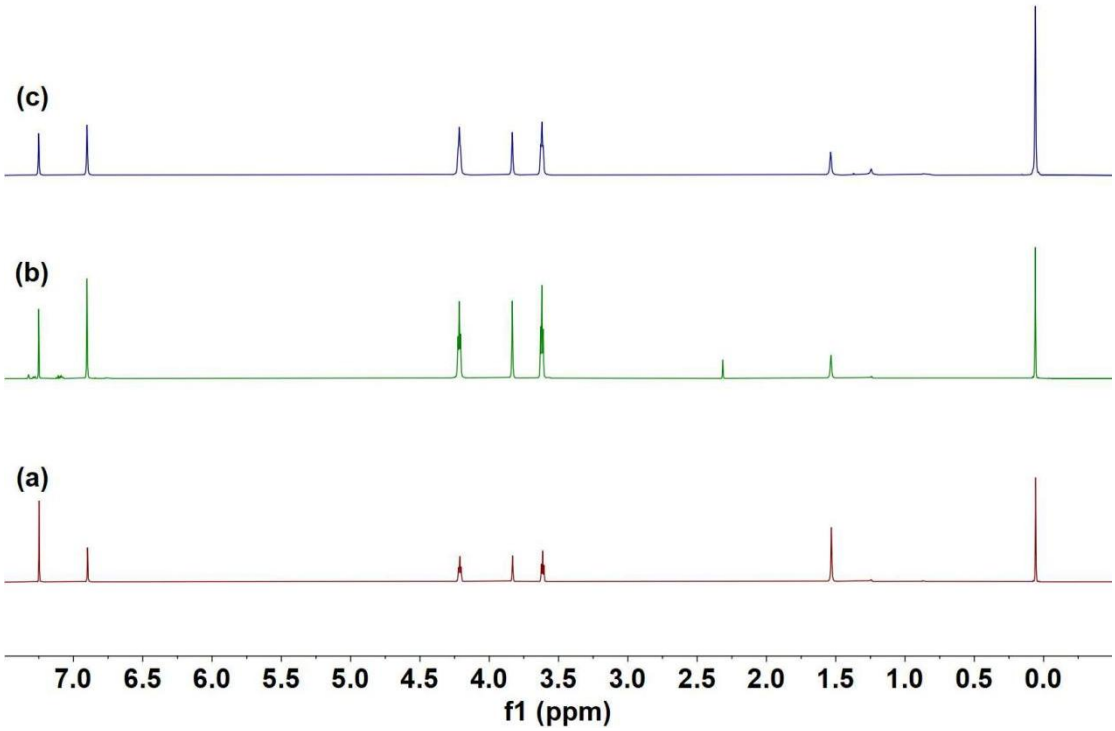

Fig. S30 ^{1}H NMR spectra (600 MHz, chloroform-*d*, 298 K): (a) original activated **BrP5** crystals; (b) **BrP5** crystals after exposure to **MBT** and **OBT** equal volume mixture vapor; (c) desolvated **BrP5** crystals.

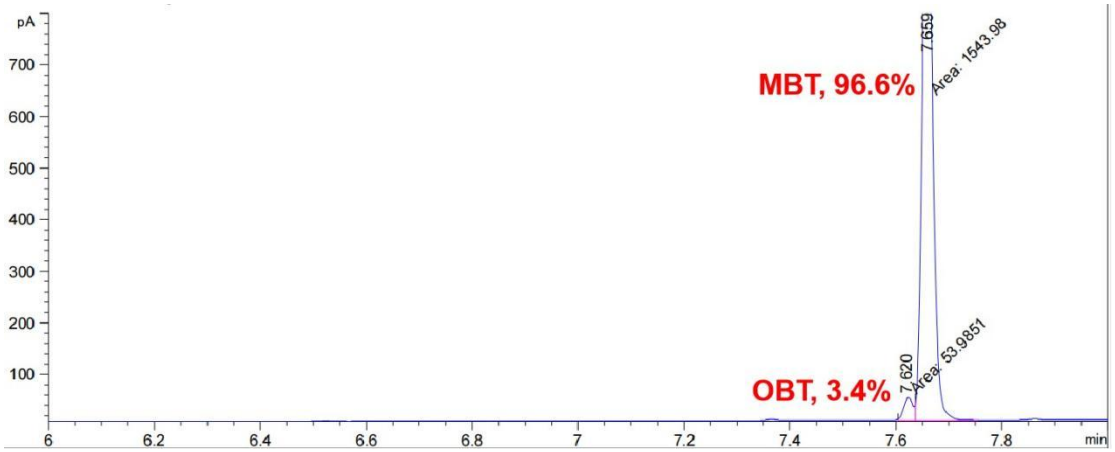

Fig. S31 The first cycle of adsorption of the equal volume mixture of **MBT** and **OBT** by **BrP5** crystals measured by GC.

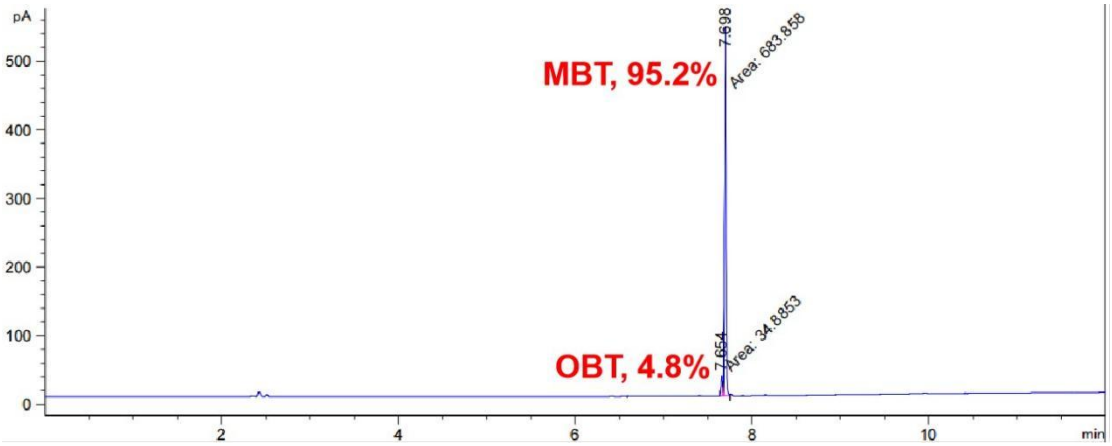

Fig. S32 The second cycle of adsorption of the equal volume mixture of **MBT** and **OBT** by **BrP5** crystals measured by GC.

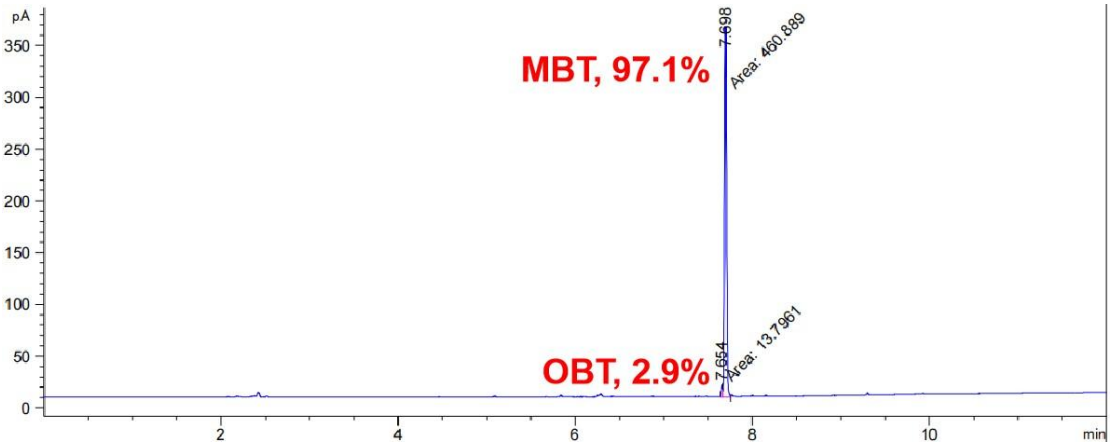

Fig. S33 The third cycle of adsorption of the equal volume mixture of **MBT** and **OBT** by **BrP5** crystals measured by GC.

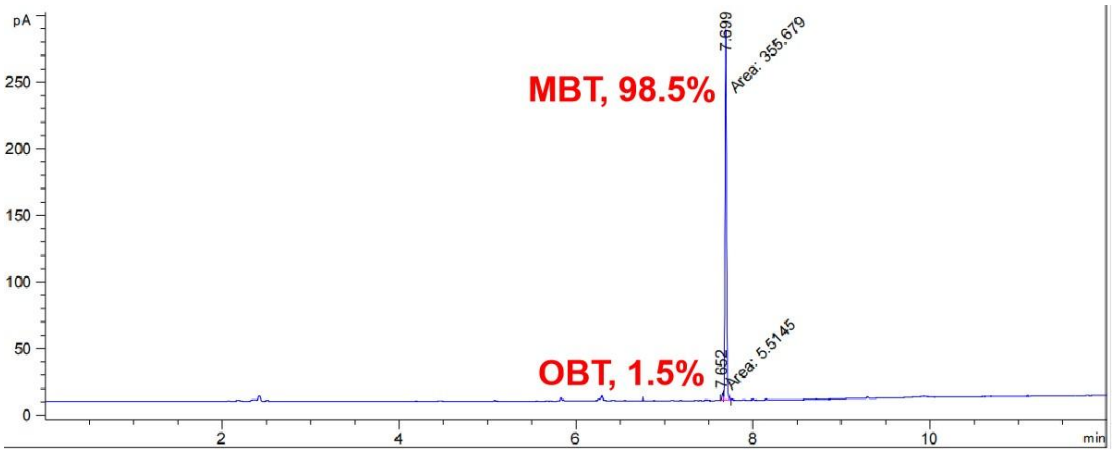

Fig. S34 The fourth cycle of adsorption of the equal volume mixture of **MBT** and **OBT** by **BrP5** crystals measured by GC.

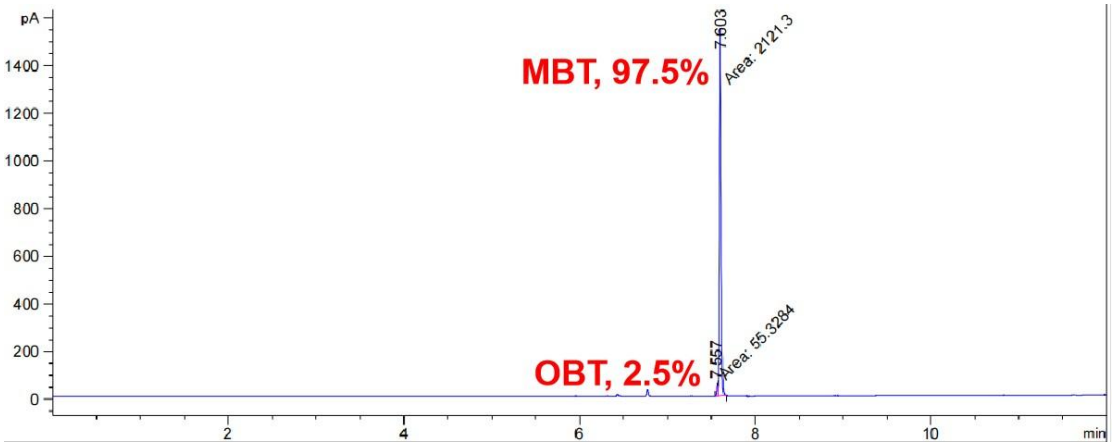

Fig. S35 The fifth cycle of adsorption of the equal volume mixture of **MBT** and **OBT** by **BrP5** crystals measured by GC.

7. References

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