Separation of Monochlorotoluene Isomers by Nonporous Adaptive Crystals of Perethylated Pillar[5]arene and Pillar[6]arene

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1. Materials

p-Diethoxybenzene (99%) was purchased and used as received. All other chemicals including *p*-chlorotoluene (**PCT**, \geq 99%), *o*-chlorotoluene (**OCT**, \geq 99%), and *m*-chlorotoluene (**MCT**, \geq 99%) were purchased and used as received. Both **EtP5** and **EtP6** were synthesized as described previously.^{S1} Activated crystalline **EtP5** and **EtP6** were referred to as **EtP5** α and **EtP6** β , respectively. Both **EtP5** α and **EtP6** β were prepared according to reported procedures.^{S2}

2. Methods

2.1. Vapor Sorption Measurement

PCT and **OCT** isomer sorption isotherms were measured via a Micromeritic 3Flex instrument. Samples were degassed under dynamic vacuum for 12 hours at 80 °C prior to each measurement. The isotherms were collected at 25 °C by monitoring the volume changes. The saturated vapor pressures of both **PCT** and **OCT** were calculated by the following equation:

$$\log P^{\rm s}_{\rm i} \,({\rm kPa}) = A - (B/(T+C))$$

where $P^{s_{i}}$ is the saturated vapor pressure of pure **PCT** or **OCT**, *T* is Kelvin temperature, *A*, *B* and *C* are Antoine constants as reported.^{S3}

2.2. Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert PRO X-ray diffractometer operating at 40 kV/40 mA using the Cu K_{a1} ($\lambda = 1.540598$ Å) and K_{a2} ($\lambda = 1.544426$ Å).

2.3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. The samples were heated at 10 $^{\circ}$ C/min using N₂ as the protective gas.

2.4. Differential Scanning Calorimetric study

Differential Scanning Calorimetric study (DSC) was carried out using a DSC Q100 analyzer (TA Instruments). The samples were heated at 10 °C/min using N₂ as the protective gas.

2.5. Single Crystal Growth

Single crystals of PCT-loaded EtP5 or EtP6 were grown by cooling-induced crystallization: 5 mg of

dry **EtP5** or **EtP6** powder were put in a small vial where 0.5 mL of **PCT** was added and the vial was heated until all the powder was dissolved. The resultant transparent solution was allowed to cool down to give nice colorless crystals. Single crystals of **OCT**-loaded **EtP6** were grown by volatilization: 5 mg of dry **EtP6** powder were put in a small vial where 0.5 mL of **OCT** was added and the vial was heated until all the powder was dissolved. The colorless crystals were got by volatilization for a few days.

2.6. Single Crystal X-ray Diffraction

Single crystal X-ray diffraction data for PCT-loaded EtP5, PCT-loaded EtP6 and OCT-loaded EtP6 were collected on a Bruker D8 VENTURE CMOS X-ray diffractometer with a graphite monochromated Mo Ka radiation ($\lambda = 0.71073$ Å).

2.7. Solution ¹H NMR Spectroscopy

¹H NMR spectra were recorded with a Bruker Avance DMX 400 spectrometer.

2.8. Gas Chromatography

Head Space Gas Chromatography (HS-GC) Analysis: HS-GC measurements were carried out using an Agilent 7890B instrument configured with an FID detector and a DB-624 column (30 m × 0.53 mm × 3.0 μ m). Samples were analyzed using headspace injections and were performed by incubating the sample at 100 °C for 10 min followed by sampling 1 mL of the headspace. The following GC method was used: the oven was programmed from 50 °C, and ramped in 10 °C min⁻¹ increments to 150 °C with 15 min hold; the total run time was 25 min; the injection temperature was 250 °C; the detector temperature was 280 °C with nitrogen, air, and make-up flow rates of 35, 350, and 35 mL min⁻¹, respectively; helium (carrier gas) flow rate was 3.0 mL min⁻¹. The samples were injected in the split mode (30:1).

3. Crystallography Data

Table S1. Experimental single crystal X-ray data for PCT-loaded or OCT-loaded pillar[n] arene structures.

Formula	(PCT) ₃ @(EtP5) ₂	PCT@EtP6
Crystallization Solvent	<i>p</i> -chlorotoluene	<i>p</i> -chlorotoluene
Wavelength [Å]	0.71073	0.71073
Collection Temperature (K)	273(2)	296(2) K
Formula	C131 H164 Cl3 O20	C73 H92 Cl O12
Formula Weight	2164.97	1196.92
Crystal System	Monoclinic	Monoclinic
Space Group	P2(1)/n	P2(1)/n
<i>a</i> [Å]	11.6711(4)	a = 11.607(3)
<i>b</i> [Å]	21.5510(6)	12.917(3)
<i>c</i> [Å]	23.8501(8)	22.363(5)
α [°]	90	90
β [°]	95.321(1)	91.310(8)
γ [°]	90	90
<i>V</i> [Å ³]	5973.0(3)	3351.9(13)
Ζ	2	2
$D_{\text{calcd}} [\text{g cm}^{-3}]$	1.204	1.186
Absorption coefficient (mm ⁻¹)	0.144	0.117
F(000)	2322.0	1286
Theta range [°]	2.96-25.00	2.00-25.47
Reflections collected / unique	30634 / 10457 [R(int) = 0.0462]	20867 / 6147 [R(int) = 0.0667]
Data / restraints / parameters	10457 / 0 / 706	6147 / 0 / 394
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0672, wR_2 = 0.1723$	$R_1 = 0.0723, wR_2 = 0.1851$
R indices (all data)	$R_1 = 0.0944, wR_2 = 0.1885$	$R_1 = 0.1492, wR_2 = 0.2287$
Goodness-of-fit on F^2	1.075	1.017
Largest difference peak and	1.817 and -1.516	0.458 and - 0.375
hole [e.A ⁻³]		
CCDC	1921756	1921759

Formula	OCT@EtP6
Crystallization Solvent	o-chlorotoluene
Wavelength [Å]	0.71073
Collection Temperature (K)	273
Formula	C73 H91 Cl O12
Formula Weight	1195.90
Crystal System	Monoclinic
Space Group	P2(1)/n
<i>a</i> [Å]	11.2674(5)
<i>b</i> [Å]	12.9976(5)
<i>c</i> [Å]	22.3812(11)
α [°]	90
β [°]	91.927(2)
γ [°]	90
V [Å ³]	3275.9(3)
Z	2
$D_{ m calcd} [m g cm^{-3}]$	1.212
Absorption coefficient (mm ⁻¹)	0.120
F(000)	1284
Theta range [°]	2.971-26.425
Reflections collected / unique	35208 / 6680 [R(int) = 0.0490]
Data / restraints / parameters	6680 / 64 / 419
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0622, wR_2 = 0.1624$
R indices (all data)	$R_1 = 0.0876, wR_2 = 0.1852$
Goodness-of-fit on F^2	1.049
Largest difference peak and	0.796 and -0.632
hole [e.A ⁻³]	
CCDC	1944144

4. Characterization of Activated EtP5 Crystals (EtP5α) and EtP6 Crystals (EtP6β)



Figure S2. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **EtP6**β.



Figure S3. Thermogravimetric analysis of activated EtP5α.



Figure S4. Thermogravimetric analysis of activated **EtP6***β*.



Figure S5. Powder X-ray diffraction pattern of EtP5α.



Figure S6. Powder X-ray diffraction pattern of EtP6β.

5. Single-Component Monochlorotoluene Isomer Adsorption Experiments

An open 5 mL vial containing 20 mg of guest-free EtP5 α or EtP6 β adsorbent was placed in a sealed 20 mL vial containing 1 mL of PCT or OCT. The crystals after absorption were heated at 50 °C under vacuum for 30 min to remove the vapor molecules on the crystal surfaces. Time-dependent EtP5 α or EtP6 β solid–vapor sorption plots were measured by completely dissolving the crystals and measuring the molar ratio of PCT or OCT to EtP6 or EtP5 by ¹H NMR every 4 hours. Thermogravimetric analysis experiments were performed using EtP5 α or EtP6 β crystals after vapor sorption.



Figure S7. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **EtP5** α after sorption of **PCT** vapor for 24 h.



Figure S8. Thermogravimetric analysis of $EtP5\alpha$ after absorption of PCT vapor for 24 h. The weight loss below 150 °C can be calculated as one PCT molecule per EtP5 molecule.



Figure S9. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **EtP5** α after sorption of **OCT** vapor for 24 h.



Figure S10. Thermogravimetric analysis of $EtP5\alpha$ after sorption of OCT vapor for 24 h.



Figure S11. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **EtP6** β after sorption of **PCT** vapor for 24 h.



Figure S12. Thermogravimetric analysis of EtP6 β after sorption of PCT vapor for 24 h. The weight loss below 150 °C can be calculated as one PCT molecule per EtP6 molecule.



Figure S13. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **EtP6** β after sorption of **OCT** vapor for 24 h. A weak signal related to protons on the methyl group of **OCT** was found, indicating the weak absorption of **EtP6** β to **OCT** vapor.



Figure S14. Thermogravimetric analysis of $EtP6\beta$ after sorption of OCT vapor for 24 h.

6. Noncovalent Interactions Analysis in Single Crystal Structures



Figure S15. Illustration of PCT-loaded EtP5 lattice: a) along *a* axis; b) along *b* axis; c) along *c* axis; d) PCT molecules at the edge centers and face centers. As shown here, every lattice contains four EtP5 molecules, four PCT molecules in the cavities of EtP5 molecules, two PCT molecules (shared with another lattice) at the face centers, and four PCT molecules (shared with three other lattices) at the edge centers. Therefore, we can know that every lattice contains four EtP5 molecules and six PCT molecules. The crystal structure formula can be termed as (PCT)₃@(EtP5)₂.

The CH··· π interactions were determined according to a reported method.^{S4,S5} (a) Case one: H is above the aromatic ring and the H– π -plane distance is shorter than 3.05 Å. (b) Case two: H is not above the aromatic ring, the angle H–C···C¹, where C¹ is the nearest sp²-carbon to H, is smaller than 60°, the dihedral angle defined by the aromatic ring and H···C¹C²···I planes, where C² is the second nearest sp²-carbon to H and I is the projection of H on the aromatic ring, is between 90° and 130° and the H–line C¹C² distance is shorter than 3.05 Å. (c) Case three: H is not above the aromatic ring, the angle H–C···C¹ is smaller than 60°, the angle H–C···C¹ A.



Figure S16. Illustration of a CH $\cdots\pi$ interaction between an ethyl group on **EtP5** and the benzene ring on **PCT**. The CH $\cdots\pi$ interaction accords with Case one. H $-\pi$ -plane distance: **A** = 2.867 Å.



Figure S17. Illustration of CH··· π interactions between two H atoms on the benzene ring of **PCT** and two coordinated benzene rings on **EtP5**. These CH··· π interactions accord with Case two. Angles H–C···C¹ (C¹ is the nearest sp2-carbon to H): 2.42°, 16.74°; dihedral angles defined by the aromatic ring and H···C¹C²···I (C² is the second nearest sp²-carbons to H and I is the projection of H on the aromatic ring) planes: 105.89°, 113.50°; H–line C¹C² distances: **A** = 2.636 Å, **B** = 2.746 Å.



Figure S18. Illustration of the hydrogen binding between an O atom on **EtP5** and an aromatic H atom on **PCT**. H…O distance: $\mathbf{A} = 2.652$ Å; C–H…O angle: $\theta = 153.95^{\circ}$.



Figure S19. Illustration of CH···Cl interaction between ethyl on **EtP5** and Cl on **PCT**. H···Cl distance: **A** = 3.147 Å; C–H···Cl angle = 137.73° .



Figure S20. Illustration of edge-to-face π -stacking interactions between EtP6 and PCT. H– π -plane distances: A = 2.821 Å, B = 2.834 Å, C = 2.788 Å, D = 2.838 Å.



Figure S21. Illustration of face-to-face π -stacking interactions between **EtP6** and **PCT**. Centroid–centroid distances: **A** = 3.937 Å, **B** = 3.923 Å; dihedral angles: $\theta = 6.27^{\circ}$, $\delta = 6.30^{\circ}$.

7. Uptake Study of *p*-Chlorotoluene in EtP5 α and EtP6 β upon Absorption of *p*-Chlorotoluene/*o*-Chlorotoluene Mixtures with Various *p*-Chlorotoluene Fractions

For each PCT/OCT mixture vapor-phase absorption experiment, an open 5 mL vial containing 4 mg of guest-free EtP5 α or EtP6 β adsorbent was placed in a sealed 20 mL vial containing 1 mL of a PCT/OCT mixture with varying PCT fraction. The temperature was maintained at 298 K or 333 K. The crystals after absorption were heated at 50 °C under vacuum for 30 min to remove the monochlorotoluene molecules adsorbed on the crystal surfaces. Uptake of PCT in EtP5 α or EtP6 β was measured by completely dissolving the crystals and measuring the molar ratio of PCT to EtP6 or EtP5 by ¹H NMR after sorption of the mixture vapor for 12 hour.

As shown in the Figures S22–S24, **EtP5** α uptakes **PCT** when the fraction of **PCT** is 0.24 at 298 K. And the starting fraction of uptaking **PCT** changed to 0.34 at 333 K. This was because the **PCT** absorption is an exothermic process, and the increase of temperature is infavorable for the absorption, which can be explained by Le Chatelier's principle.^{S6}

However, a similar phenomenon was not observed for the adsorption of **PCT** into **EtP6** due to the strong complexation between **PCT** and **EtP6** (Figures S25–S27). Besides, a weak signal of protons on **OCT** was observed when the fraction of **OCT** was >0.80. There are two reasons for this phenomenon. At first, the larger cavity of **EtP6** can also accommodate **OCT**, which was proved by the **OCT**-loaded **EtP6** single crystal structure (Figure 3d). Secondly, when the fraction of **OCT** was >0.80, **EtP6** crystals were also surrounded by **OCT** molecules.



Figure S22. ¹H NMR spectra (400 MHz, chloroform-*d*, 298 K) of EtP5 α after sorption of the vapors of PCT/OCT mixtures with various PCT fractions for 12 h at 298 K.



Figure S23. ¹H NMR spectra (400 MHz, chloroform-*d*, 298 K) of EtP5 α after sorption of the vapors of PCT/OCT mixtures with various PCT fractions for 12 h at 333 K.



Figure S24. Changes of the PCT uptake in EtP5 α after sorption of the vapors of PCT/OCT mixtures with various PCT fractions for 12 h at different temperatures.



Figure S25. ¹H NMR spectra (400 MHz, chloroform-*d*, 298 K) of EtP6 β after sorption of the vapors of PCT/OCT mixtures with various PCT fractions for 12 h at 298 K.



Figure S26. ¹H NMR spectra (400 MHz, chloroform-*d*, 298 K) of **EtP6** β after absorption to the vapors of **PCT/OCT** mixtures with various **PCT** fractions for 12 h at 333 K.



Figure S27. Changes of the PCT uptake in EtP6 β after sorption of the vapors of PCT/OCT mixtures with various PCT fractions for 12 h at different temperatures.

8. Differential Scanning Calorimetric Study of *p*-Chlorotoluene Loaded EtP5α and EtP6β



Figure S28. DSC plot of PCT-loaded EtP5α.



Figure S29. DSC plot of PCT-loaded EtP6β.

9. Separation of *p*-Chlorotoluene from Monochlorotulene Isomer Mixtures by EtP5a and EtP6β

9.1. Separation of PCT from a PCT/OCT Equimolar Mixture by EtP5α and EtP6β

An open 5 mL vial containing 20 mg of guest-free **EtP5** α or **EtP6** β adsorbent was placed in a sealed 20 mL vial containing 1 mL of a **PCT/OCT** equimolar mixture.

Time-dependent EtP5 α or EtP6 β solid-vapor sorption plots were measured by completely dissolving the crystals and measuring the molar ratio of PCT or OCT to EtP6 or EtP5 every 4 hours by ¹H NMR spectroscopy. Thermogravimetric analysis experiments were performed using EtP5 α or EtP6 β after absorption of the PCT/OCT equimolar mixture vapor for 48 h. The relative uptakes of PCT and OCT in EtP5 α or EtP6 β were measured by heating to release the adsorbed vapor and detecting the relative amounts of monochlorotoluene isomers in the released vapor using gas chromatography. Before measurements, the crystals were heated at 50 °C under vacuum for 30 min to remove the surface-physically adsorbed monochlorotoluene molecules.



Figure S30. Time-dependent EtP5 α solid-vapor sorption plot for a PCT/OCT equimolar mixture vapor.



Figure S31. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of EtP5 α after sorption of the PCT/OCT equimolar mixture vapor for 48 h.



Figure S32. Powder X-ray diffraction patterns of EtP5: (I) EtP5 α upon absorption of PCT vapor for 48 h (blue); (II) EtP5 α upon absorption of the PCT/OCT equimolar mixture vapor for 48 h (red).



Figure S33. Thermogravimetric analysis of EtP5 α after absorption of the PCT/OCT equimolar mixture vapor for 48 h. The weight loss below 150 °C can be calculated as one PCT molecule per EtP5 molecule.



Figure S34. Relative uptakes of PCT and OCT adsorbed in EtP5 α after absorption of the PCT/OCT equimolar mixture vapor for 48 hours using head space gas chromatography.



Figure S35. Time-dependent EtP6 β solid-vapor sorption plot in EtP6 α for the PCT/OCT equimolar mixture.



Figure S36. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of EtP6 β after sorption of the PCT/OCT equimolar mixture vapor for 48 h.



Figure S37. Powder X-ray diffraction patterns of **EtP6**: (I) **EtP6** β upon absorption of **PCT** vapor for 48 h (blue); (II) **EtP6** β upon absorption of the **PCT/OCT** equimolar mixture vapor for 48 h (red).



Figure S38. Thermogravimetric analysis of $EtP6\beta$ after absorption of the PCT/OCT equimolar mixture vapor for 48 h. The weight loss below 150 °C can be calculated as one PCT molecule per EtP6 molecule.



Figure S39. Relative uptakes of PCT and OCT adsorbed in EtP6 β after absorption of the PCT/OCT equimolar mixture vapor for 48 h using head space gas chromatography.

9.2. Separation of PCT from a Mixture Composed of PCT : OCT : MCT = 50 : 49 : 1 (v : v : v) by EtP5 α and EtP6 β

An open 5 mL vial containing 20 mg of guest-free EtP5 α or EtP6 β adsorbent was placed in a sealed 20 mL vial containing 1 mL of a mixture composed of PCT : OCT : MCT = 50 : 49 : 1 (v : v : v). The relative uptakes of PCT, OCT and MCT in EtP5 α or EtP6 β were measured by heating to release the adsorbed vapor and detecting the relative amounts of monochlorotoluene isomers in the released vapor using gas chromatography. Before measurements, the crystals were heated at 50 °C for 30 min to remove the surface-physically adsorbed monochlorotoluene molecules.



Figure S40. Relative uptakes of PCT, OCT and MCT adsorbed in EtP5 α after absorption of a PCT, OCT and MCT mixture (v : v : v = 50 : 49 : 1) vapor for 48 hours using head space gas chromatography.



Figure S41. Relative amounts of PCT and OCT adsorbed in EtP5 α after saturated absorption of the PCT, OCT and MCT mixture (v : v : v = 50 : 49 : 1) vapor.



Figure S42. Relative uptakes of PCT, OCT, and MCT adsorbed in EtP6 β after absorption of the PCT, OCT and MCT mixture (v : v : v = 50 : 49 : 1) vapor for 48 hours using head space gas chromatography.



Figure S43. Relative amounts of PCT and OCT adsorbed in EtP6 β after saturated absorption of the PCT, OCT and MCT mixture (v : v : v = 50 : 49 : 1) vapor.

10. Recyclability of EtP5 α and **EtP6** β



Figure S44. Thermogravimetric analysis of **PCT**-loaded **EtP5** α after heating at 100 °C under vacuum for 2 h.



Figure S45. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **PCT**-loaded **EtP5** α after heating at 100 °C under vacuum for 2 h.



Figure S46. Thermogravimetric analysis of PCT-loaded EtP6 β after heating at 100 °C under vacuum for 2 h.



Figure S47. ¹H NMR spectrum (400 MHz, chloroform-*d*, 298 K) of **PCT**-loaded **EtP6** β after heating at 100 °C under vacuum for 2 h.



Figure S48. Powder X-ray diffraction patterns of **EtP5**: (I) original **EtP5** α (green); (II) **EtP5** α after heating at 100 °C under vacuum for 2 h (red); (III) **EtP5** α after 5 cycles (blue).



Figure S49. Powder X-ray diffraction patterns of **EtP6**: (I) original **EtP6** β (green); (II) **EtP6** β after heating at 100 °C under vacuum for 2 h (red); (III) **EtP6** β after 5 cycles (blue).

11. ¹H NMR spectra for Host–Guest Interactions Study in Solution

The complexation between hosts and guests was investigated by ¹H NMR spectroscopy. Results showed that no chemical shift change happened to protons on **PCT** and **OCT** after addition of host molecules. And there was no chemical shift change found for protons on both **EtP5** and **EtP6**. These results indicated that there was no host–guest interaction between host **EtP5** or **EtP6** and guest **PCT** or **OCT** in solution.



Figure S50 Chemical structure of PCT, OCT, EtP5 and EtP6.



Figure S51 ¹H NMR spectra (400 MHz, CDCl₃, 293 K): (a) PCT (5.00 mM); (b) PCT (5.00 mM) + EtP5 (5.00 mM); (c) EtP5 (5.00 mM); (d) OCT (5.00 mM) + EtP5 (5.00 mM); (e) OCT (5.00 mM).



Figure S52 ¹H NMR spectra (400 MHz, CDCl₃, 293 K): (a) **PCT** (5.00 mM); (b) **PCT** (5.00 mM) + **EtP6** (5.00 mM); (c) **EtP6** (5.00 mM); (d) **OCT** (5.00 mM) + **EtP6** (5.00 mM); (e) **OCT** (5.00 mM).

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