Efficient separation of xylene isomers by nonporous adaptive crystals of hybrid[3]arene in both vapor and liquid phases

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Electronic Supplementary Information (30 pages)

1. *Materials*

All chemicals, including *ortho*-xylene (***o*X**), *meta*-xylene (***m*X**) and *para*-xylene (***p*X**), were purchased and used as received. Hybrid[3]arene (**H**) was synthesized as described previously.[1] Activated crystalline **H** (**H*α***) was recrystallized from acetone and dried under vacuum at 120 °C overnight.[2]

Table S1. Physical properties of xylene isomers.

Xylene isomers	Boiling points (℃)	Melting points (℃)	Kinetic diameters (Å)
***o*X**	144.40	-25.2	6.5
***m*X**	139.10	-47.9	6.4
***p*X**	138.50	13.2	5.8

2. Methods

2.1. Solution NMR

Solution ^{1}H NMR spectra were recorded at 600 MHz using a Bruker Avance 600 NMR spectrometer.

2.2. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultimate-IV X-ray diffractometer operating at 40 kV/30 mA using the Mo Kα line (λ = 1.5418 Å). Data were measured over the range of 5−40° in 5°/min steps over 7 min.

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 °C/min using N_2 as the protective gas.

2.4. Single crystal growth

Single crystals of ***o*X@H** and ***m*X@H** were grown by slow evaporation: 3.00 mg of dry **H*α*** powders were put in a small vial where 1 mL of ***o*X** or ***m*X** was added. Then adding chloroform until all **H*α*** powders were dissolved. The resultant transparent solution was allowed to evaporate slowly to give nice colorless crystals in 2 to 3 days.

2.5. Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected on a Bruker D8 VENTURE CMOS X-ray

diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

2.6. Gas chromatography

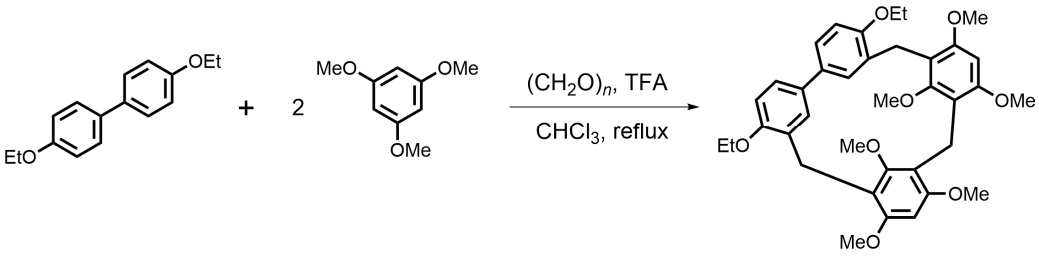
Head Space Gas Chromatography (HS-GC) Analysis: HS-GC measurements were carried out using an Agilent 7890B instrument with an FID detector and a DB-624 column (30 m × 0.53 mm × 3.0 μm). Samples were analyzed using headspace injections and were performed by incubating the sample at 100 °C for 10 min followed 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; the helium (carrier gas) flow rate was 3.0 mL min^{-1}. The samples were injected in the split mode (30:1).

2.7 Density functional theory (DFT) calculations

All calculations were performed by DFT using the B3LYP hybrid function combined with 6-31G(dp) basis set under Gaussian G09. Using single-crystal structures as input files, IGM analyses were carried out by Multiwfn 3.6 program through function 20 (visual study of weak interaction) and visualized using Visual Molecular Dynamics software.

3. Synthesis of hybrid[3]arene ***H***

Scheme S1. Synthesis route to hybrid[3]arene



A mixture of 1 equiv. of 4,4'-biphenol diethyl ether, 2 equiv. of 1,3,5-trimethoxybenzene, 3 equiv. of paraformaldehyde, and a catalytic amount of trifluoroacetic acid (TFA) was refluxed in chloroform for 30 min. The reaction mixture was cooled to room temperature, and an excess of saturated aqueous Na_2CO_3 was added to neutralize TFA. After purification by column chromatography, hybrid[3]arene was isolated in 28% yield as a white solid.

4. Crystallography data

Table S2. Experimental single crystal X-ray data for ***o*X@H**.

Formula	***o*X@H**
Crystallization Solvent	*ortho*-xylene
Collection Temperature (K)	170.0
Formula	$C_{45}H_{52}O_8$
Formula Weight	720.86
Crystal System	Triclinic
Space Group	*P*-1
a [Å]	10.9489(8)
b [Å]	13.1954(8)
c [Å]	15.6147(10)
α [°]	110.605(3)
β [°]	99.658(3)
γ [°]	107.053(2)
V [Å^3]	1924.0(2)
Z	2
D_{calcd} [g cm^{-3}]	1.244
Absorption coefficient (mm^{-1})	0.084
F(000)	772
Crystal size/mm^3	0.48 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)
Theta range/°	4.242 to 53.602
Index ranges	$-13 \le h \le 13$, $-16 \le k \le 16$, $-19 \le l \le 19$
Reflections collected	8156
Independent reflections	8156 [R_{int} = 0.0779, R_{sigma} = 0.0636]
Data/restraints/parameters	8156/0/489
CCDC	2214282

Table S3. Experimental single crystal X-ray data for ***m*X@H**.

Formula	***m*X@H**
Crystallization Solvent	*meta*-xylene
Collection Temperature (K)	$C_{45}H_{52}O_8$
Formula	720.86
Formula Weight	170.0
Crystal System	triclinic
Space Group	*P*-1
a [Å]	10.8496(4)
b [Å]	13.1599(5)
c [Å]	15.6652(7)
α [°]	109.8910(10)
β [°]	97.3970(10)
γ [°]	105.8220(10)
V [Å^3]	1961.96(14)
Z	2
D_{calcd} [g cm^{-3}]	1.220
Adsorption coefficient (mm^{-1})	0.083
F(000)	772.0
Crystal size/mm^3	0.48 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)
Theta range/°	4.978 to 54.286
Index ranges	$-13 \le h \le 13$, $-16 \le k \le 16$, $-20 \le l \le 20$
Reflections collected	41841
Independent reflections	8662 [R_{int} = 0.0396, R_{sigma} = 0.0348]
Data/restraints/parameters	8662/0/488
CCDC	2214284

*5. Characterization of nonporous adaptive crystals of **H** (**Hα**)*

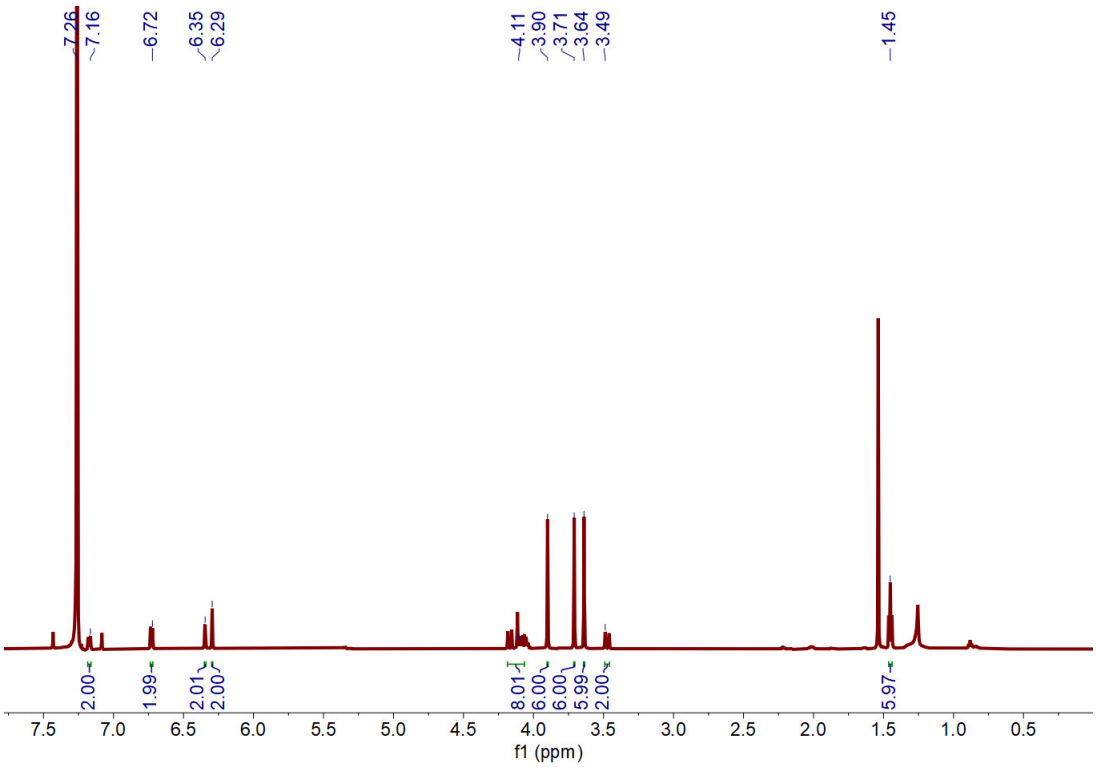


Fig. S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **Hα**.

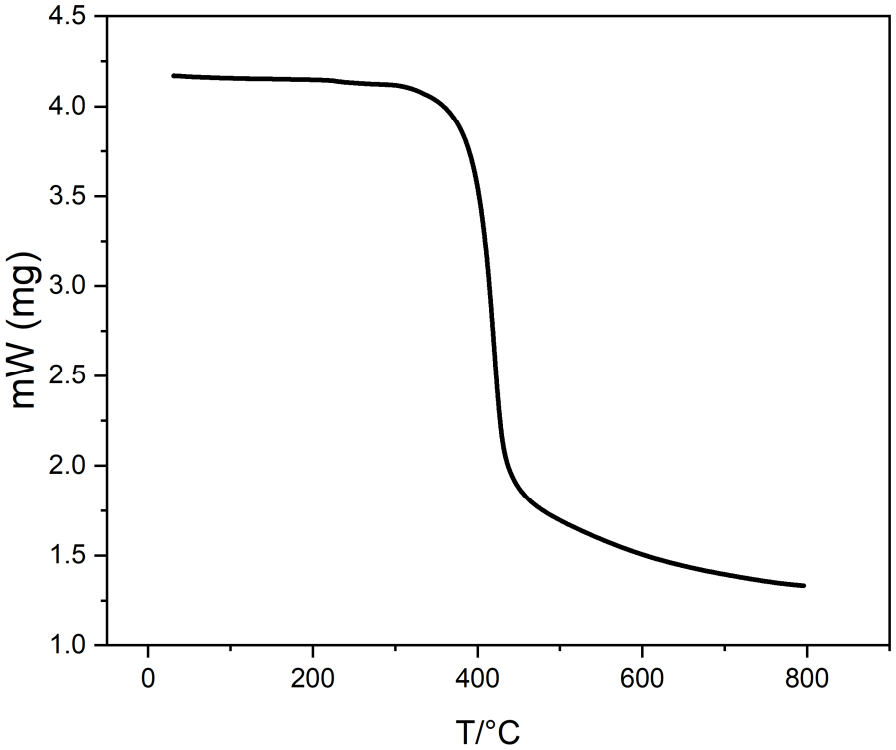


Fig. S2. Thermogravimetric analysis of **Hα**.

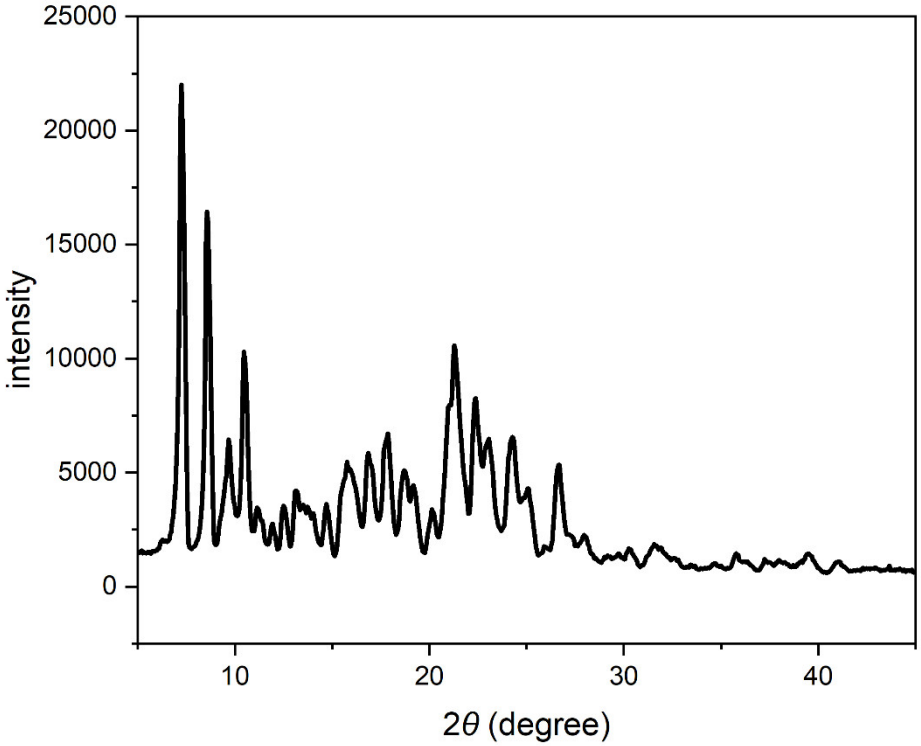


Fig. S3. Powder X-ray diffraction pattern of **H*α***.

*6. Adsorption experiments of **Hα** for single-component xylene isomers*

^{1}H NMR experiments were performed by dissolving **H*α*** after adsorption of single-component xylene isomers vapors in $CDCl_3$. TGA profiles were recorded using **H*α*** after adsorption of single-component xylene isomers vapors.

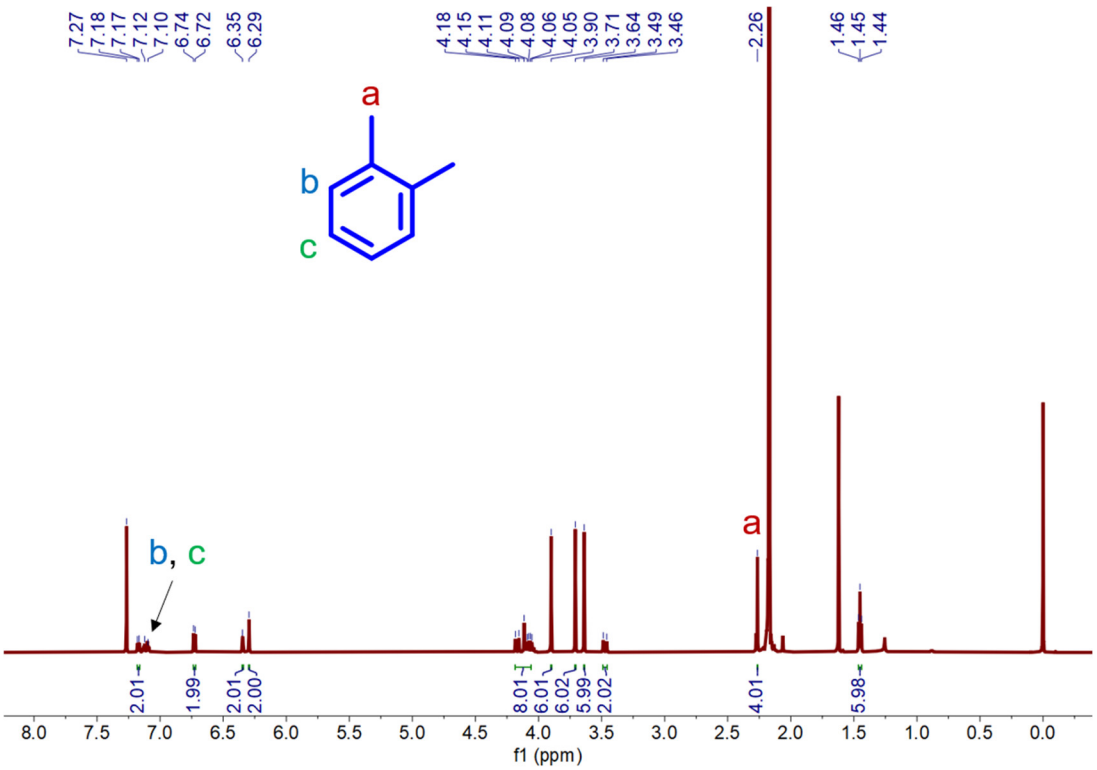


Fig. S4. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of ***o*X** vapor for 12 h.

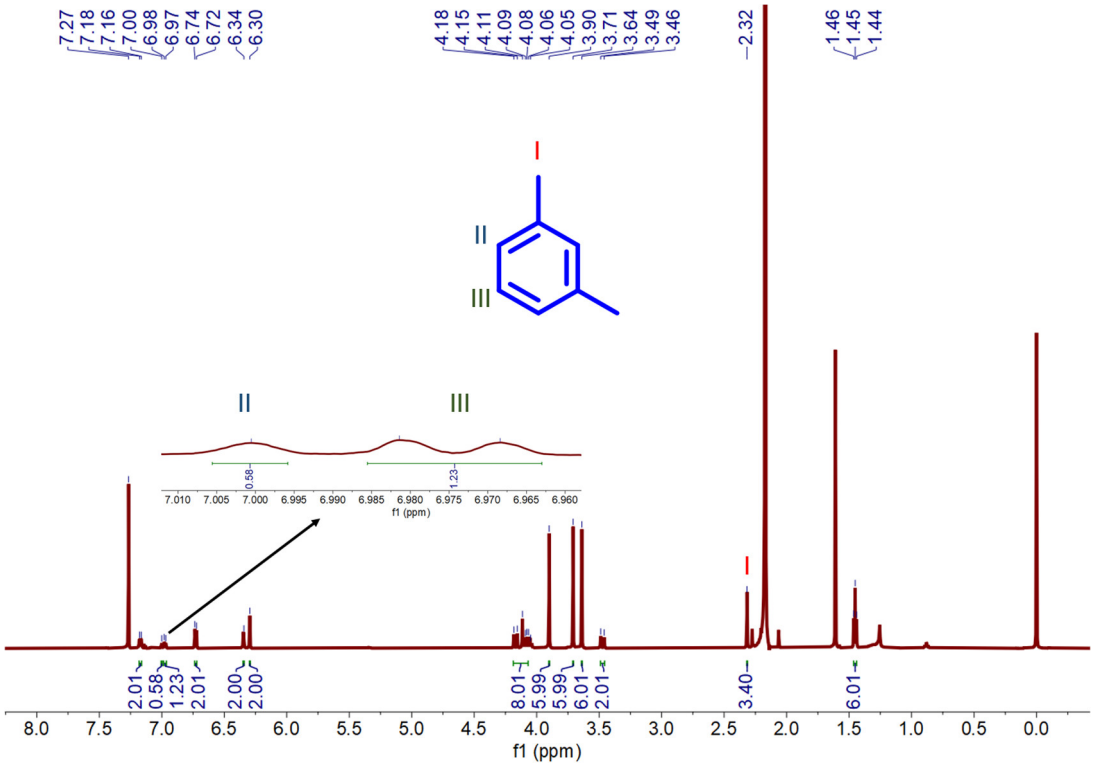


Fig. S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of ***m*X** vapor for 12 h.

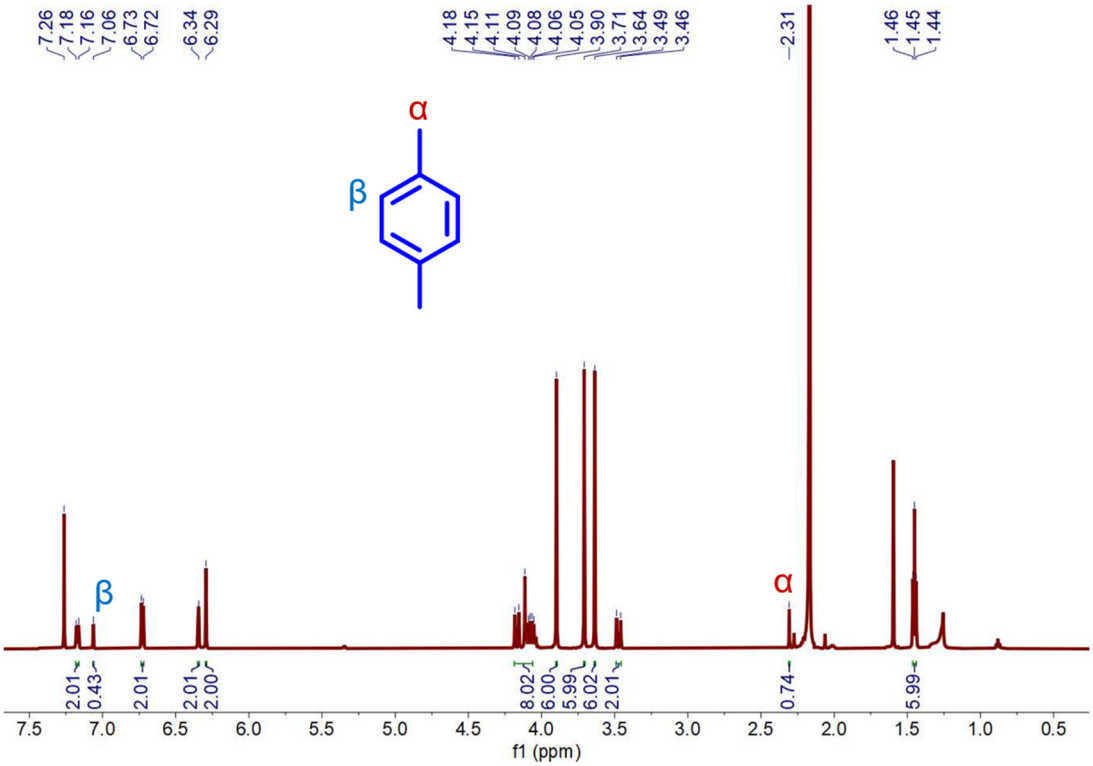


Fig. S6. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of ***p*X** vapor for 12 h.

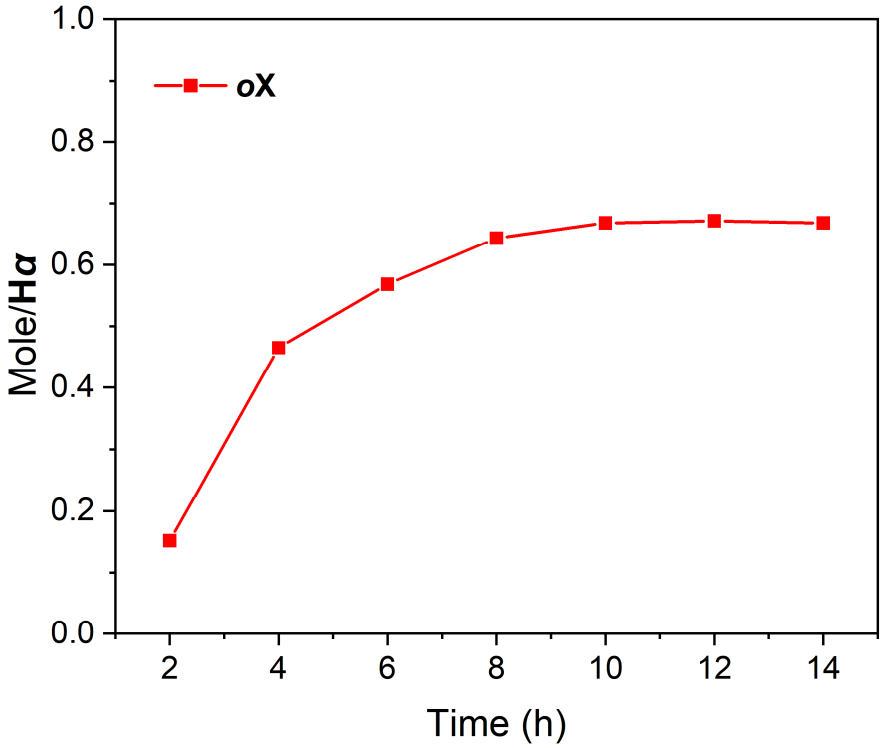


Fig. S7. Time-dependent vapor−solid adsorption plots of **H*α*** for single-component ***o*X** vapor.

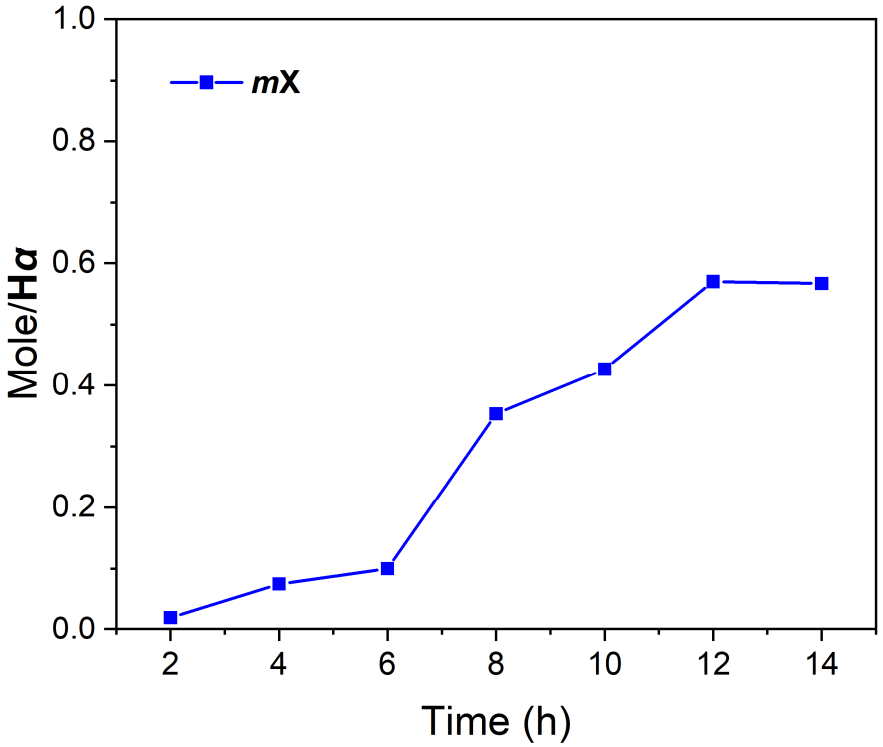


Fig. S8. Time-dependent vapor−solid adsorption plots of **H*α*** for single-component ***m*X** vapor.

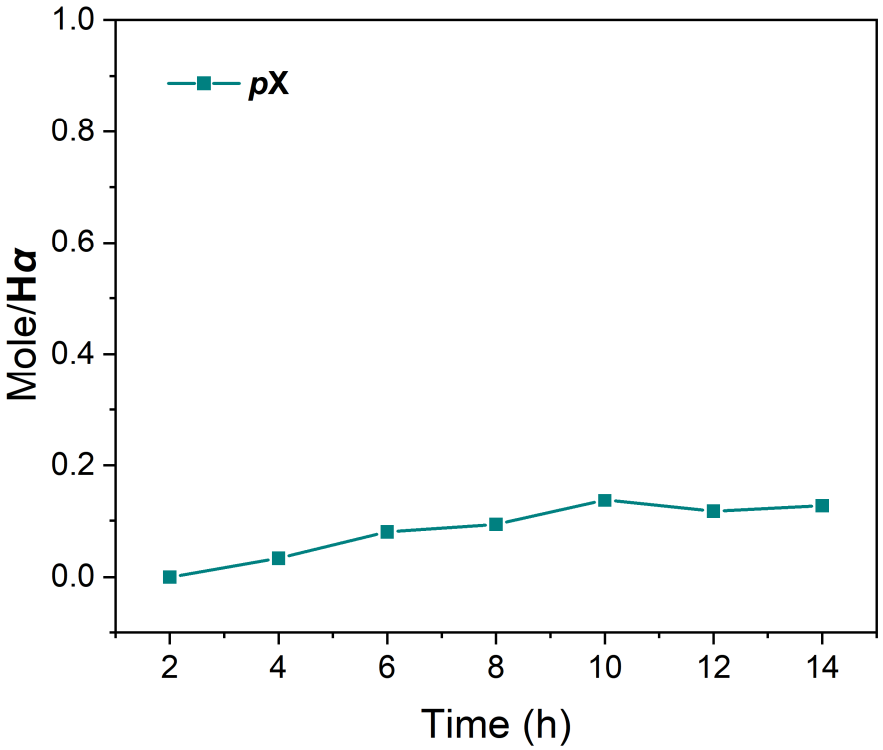


Fig. S9. Time-dependent vapor−solid adsorption plots of **H*α*** for single-component ***p*X** vapor.

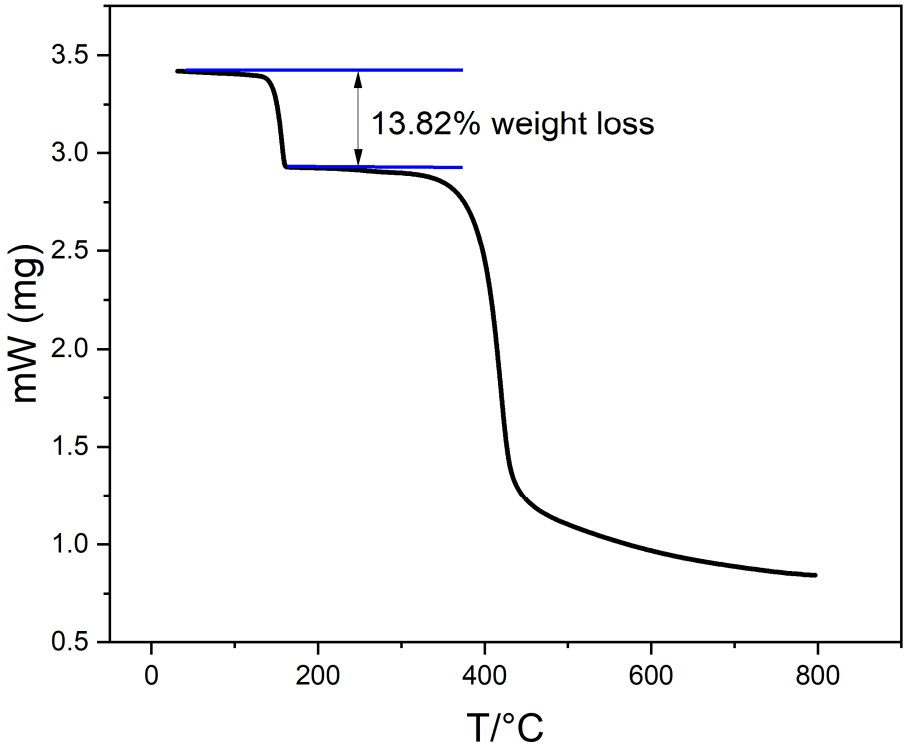


Fig. S10. Thermogravimetric analysis of **H*α*** after adsorption of ***o*X** vapor for 12 h. The weight loss at 150 °C can be calculated as 0.9 ***o*X** molecule per **H*α*** molecule.

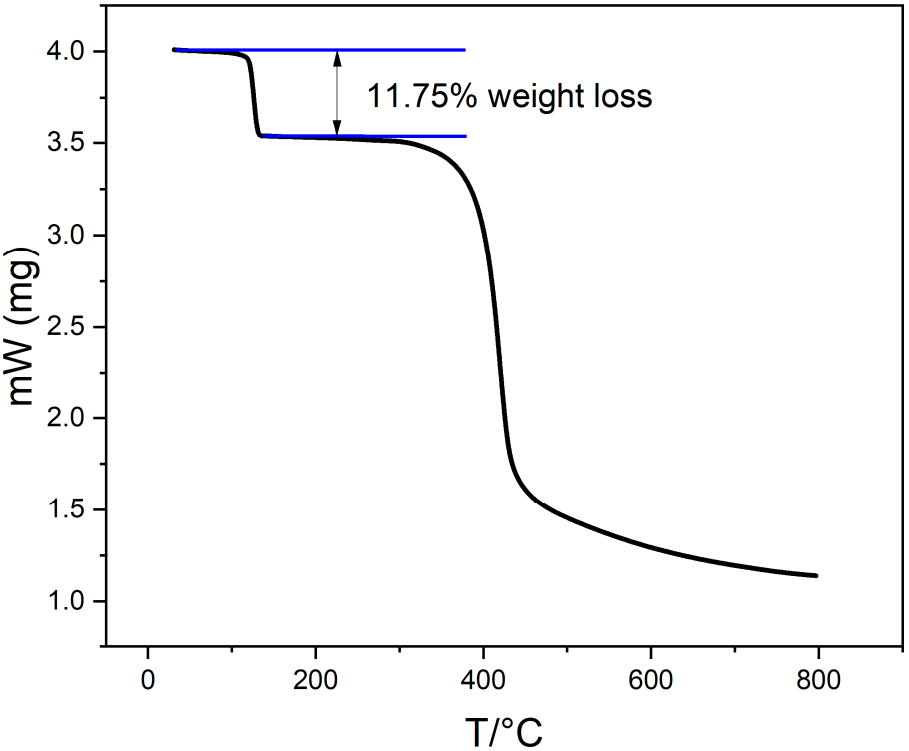


Fig. S11. Thermogravimetric analysis of **H*α*** after adsorption of ***m*X** vapor for 12 h. The weight loss at 150 °C can be calculated as 0.8 ***m*X** molecule per **H*α*** molecule.

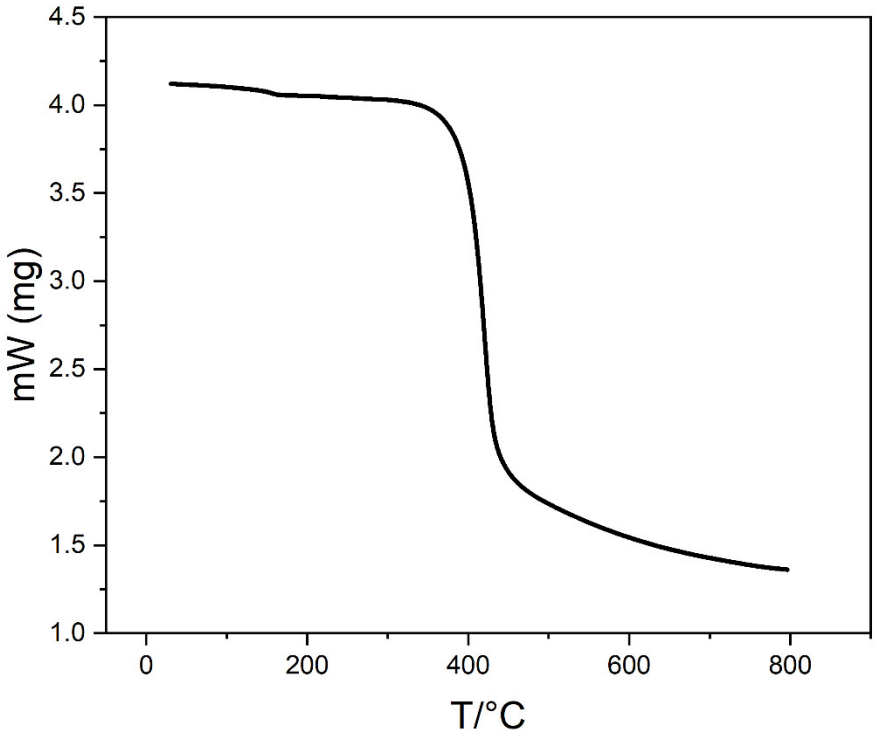


Fig. S12. Thermogravimetric analysis of **H*α*** after adsorption of ***p*X** vapor for 12 h.

7. Noncovalent interactions analysis in single crystal structures of host–guest complexes

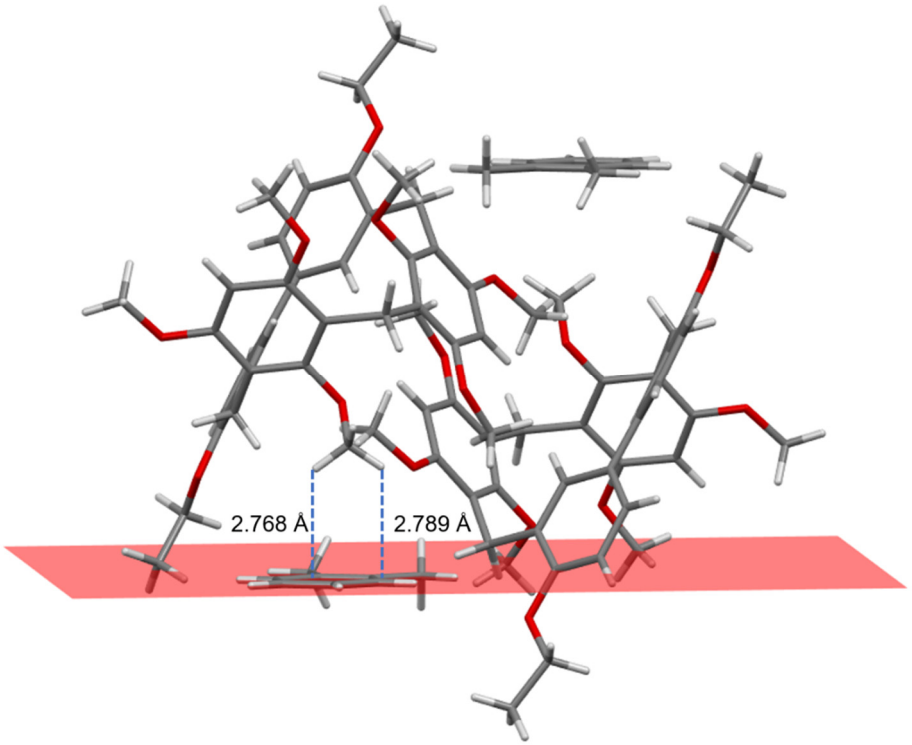


Fig. S13. Single crystal of ***o*X@H**: illustration of C–H···π interaction between two hydrogen atoms on the methyl group of **H** and the benzene ring of ***o*X**, the distances between hydrogen atoms and benzene ring were 2.768 Å and 2.789 Å.

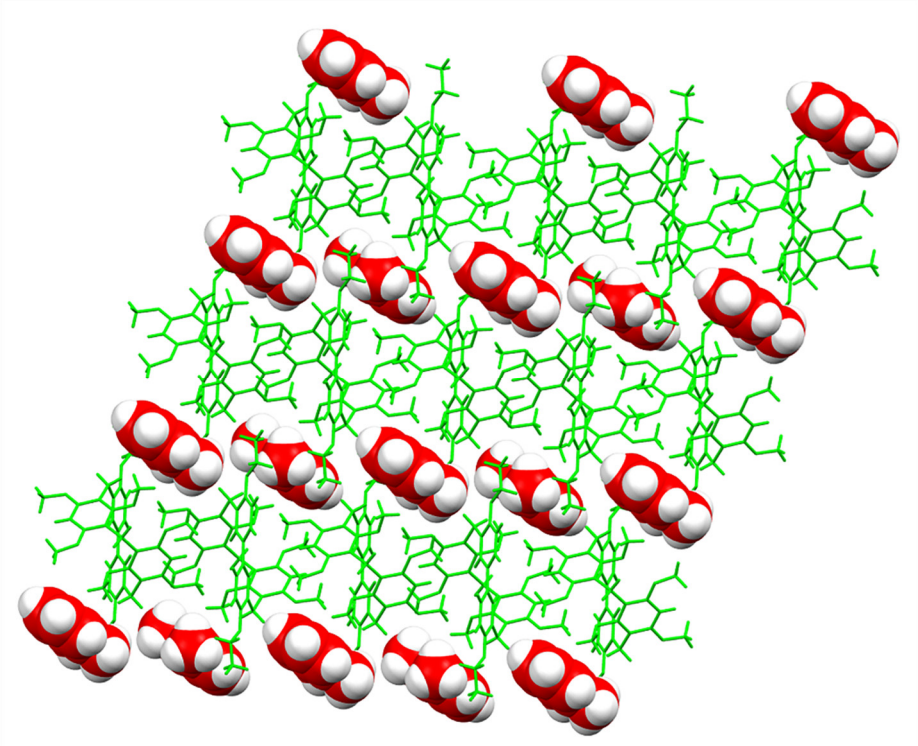


Fig. S14. Single crystal of ***o*X@H**, ***o*X** molecules were in the channels formed by **H**.

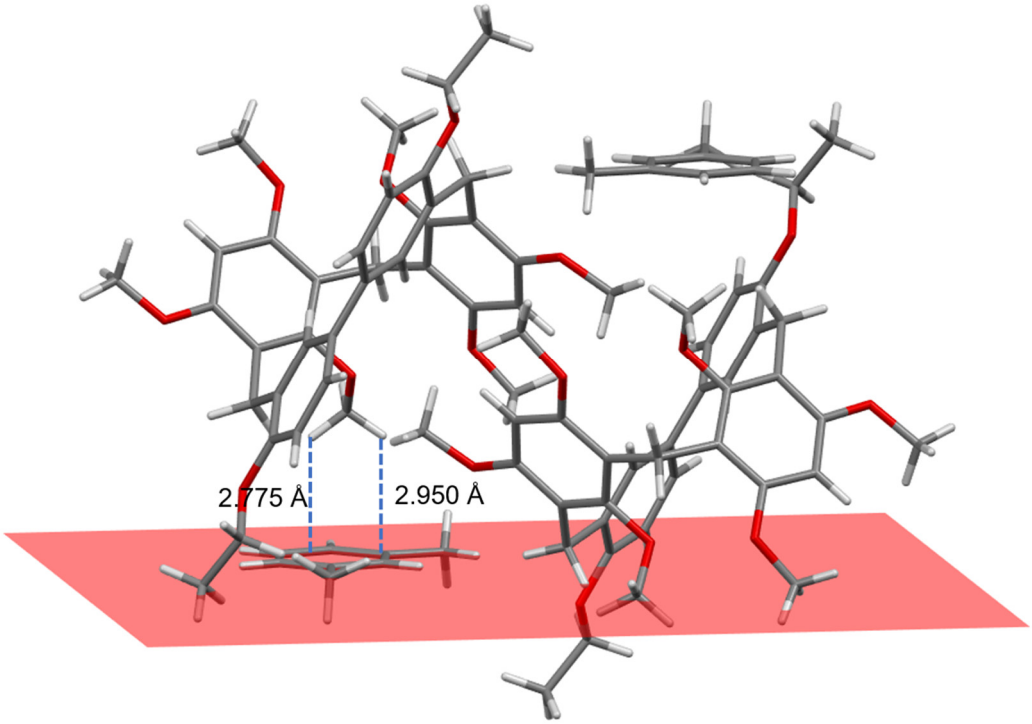


Fig. S15. Single crystal of ***m*X@H**: illustration of C–H···π interaction between two hydrogen atoms on the methyl group of **H** and the benzene ring of ***o*X**, the distances between hydrogen atoms and benzene ring were 2.775 Å and 2.950 Å.

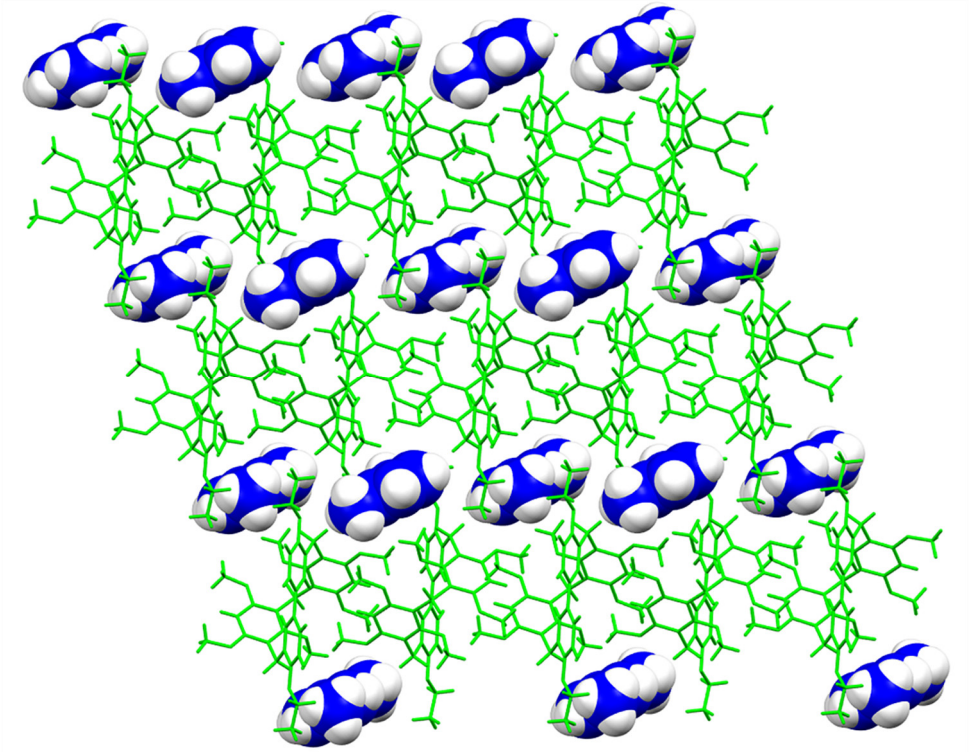


Fig. S16. Single crystal of ***m*X@H**, ***m*X** molecules were in the channels formed by **H**.

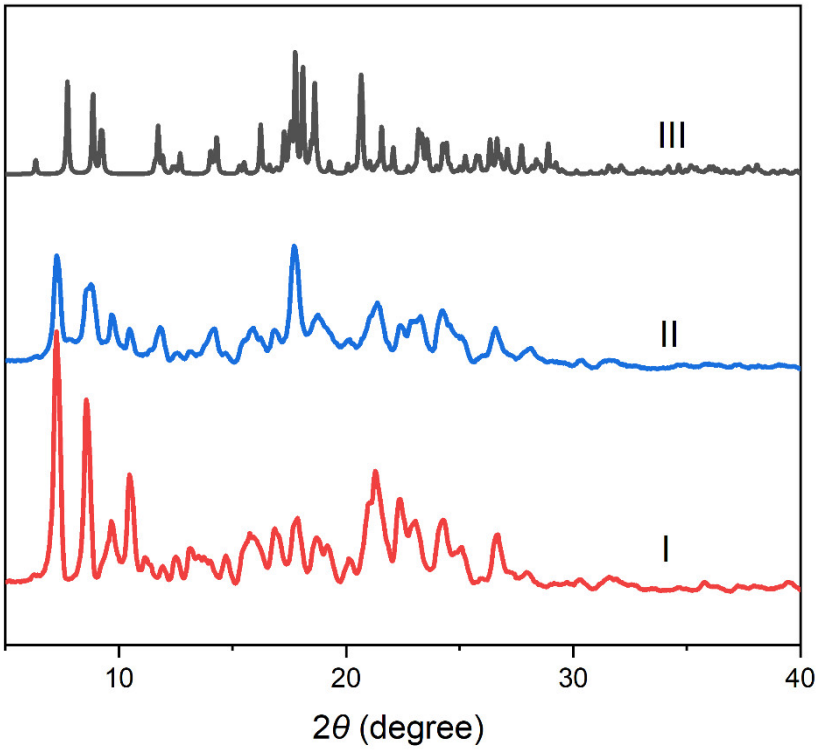


Fig. S17. PXRD patterns of **H*α***: (I) original **H*α***; (II) **H*α*** after adsorption of ***o*X** vapor; (III) simulated from single crystal of ***o*X@H**.

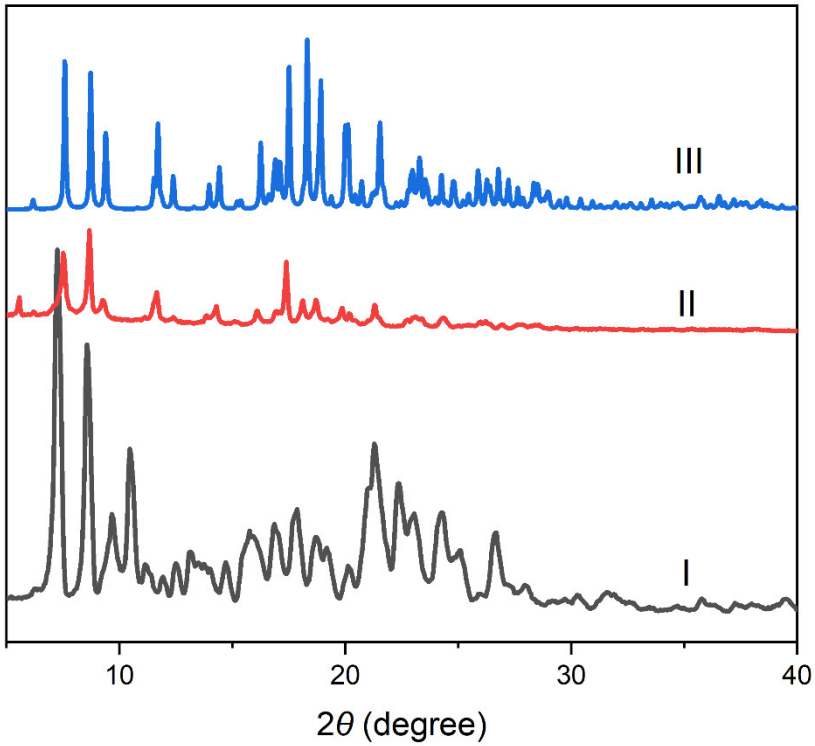


Fig. S18. PXRD patterns of **H*α***: (I) original **H*α***; (II) **H*α*** after adsorption of ***m*X** vapor; (III) simulated from single crystal of ***m*X@H**.

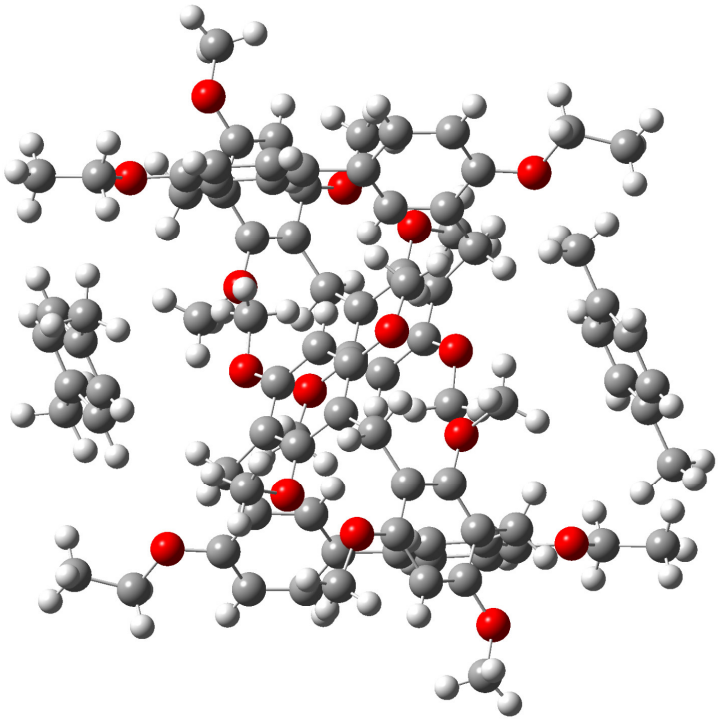


Fig. S19. Structure of ***p*X@H** based on DFT calculation.

*8. Uptake from the binary mixture of xylene isomers by **H*α***

An open 5 mL vial containing 2.00 mg of guest-free **H*α*** was placed in a sealed 20 mL vial containing 1 mL of the mixture of ***o*X** and ***m*X** (*v*:*v* = 1:1). Uptake in **H*α*** was measured hour by hour by completely dissolving the crystals and measuring the ratio of ***o*X** or ***m*X** to **H*α*** by ^{1}H NMR. The relative uptakes of ***o*X**

and ***m*X** vapors in **H*α*** were also measured by heating the crystals to release the adsorbed vapor and detecting the relative amounts of ***o*X** and ***m*X** in the released vapor using head space gas chromatography.

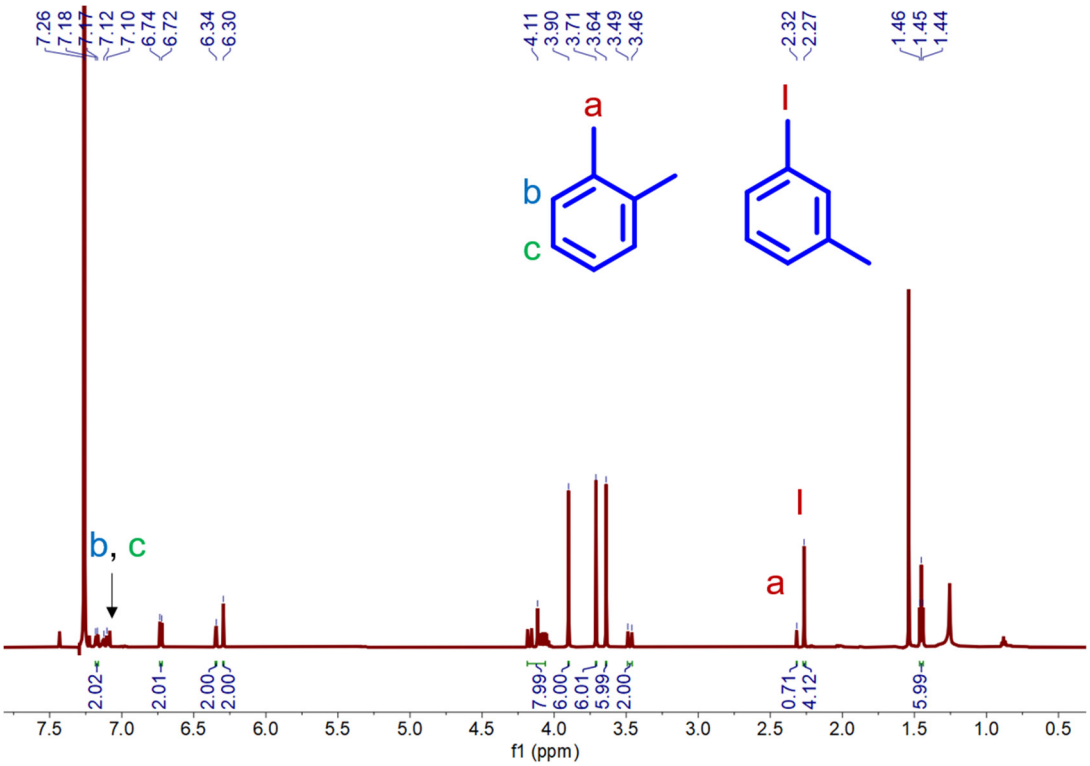


Fig. S20. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the mixture of ***o*X**/***m*X** (*v*:*v* = 1:1) vapor for 12 h.

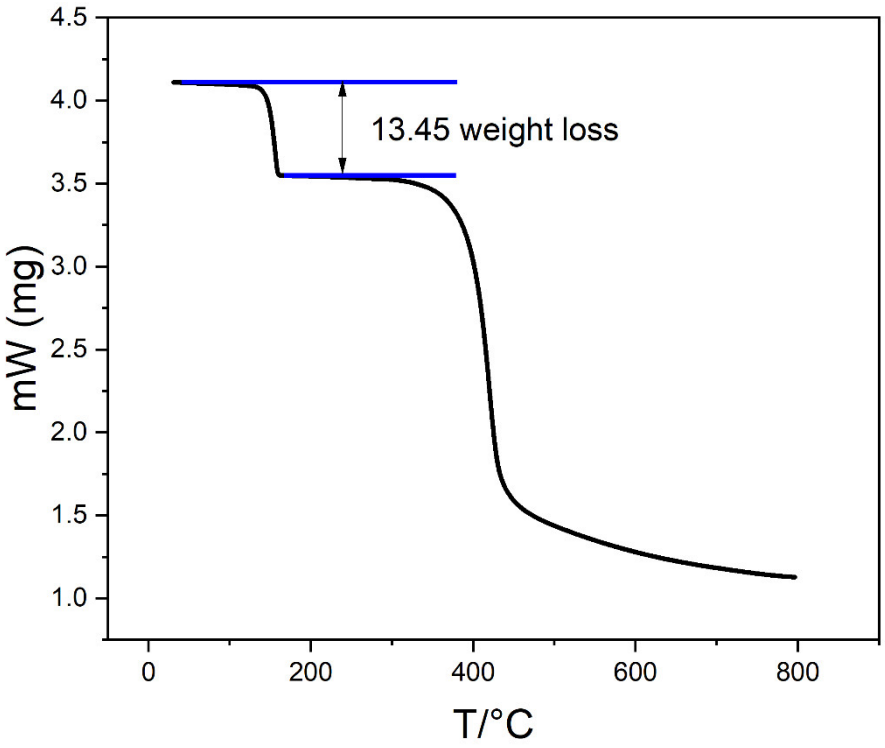


Fig. S21. Thermogravimetric analysis of **H** after sorption of the vapor mixture of ***o*X** and ***m*X** for 14 h. The weight loss at 150 °C can be calculated as 0.9 ***o*X** molecule per **H** molecule.

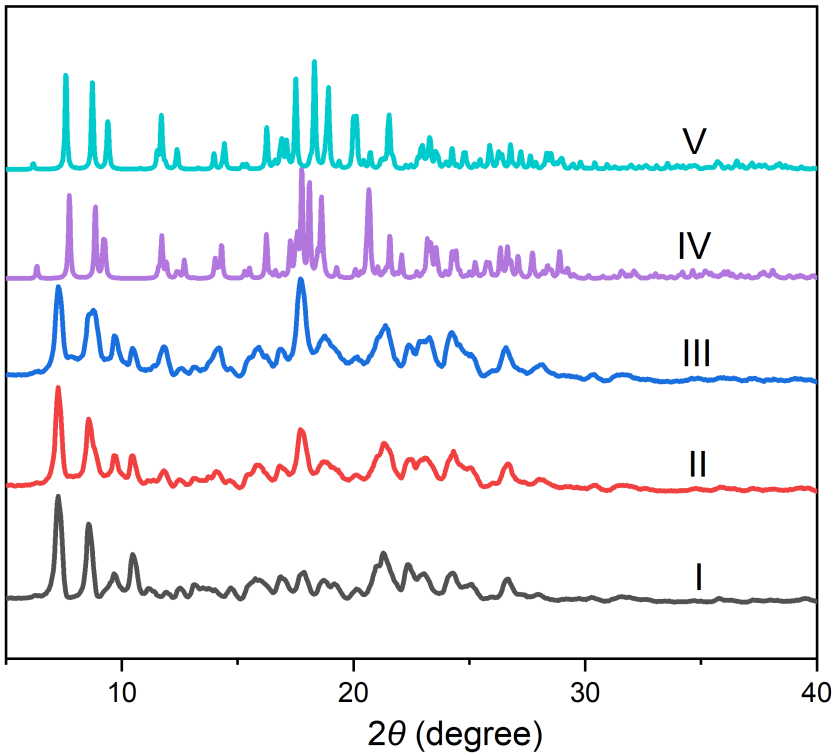


Fig. 22. PXRD patterns of **H*α***: (I) original **H*α***; (II) **H*α*** after adsorption of the mixture of ***o*X** and ***p*X**; (III) **H*α*** after adsorption of ***o*X**; (IV) simulated from single crystal of ***o*X@H**; (V) simulated from single crystal of ***m*X@H**.

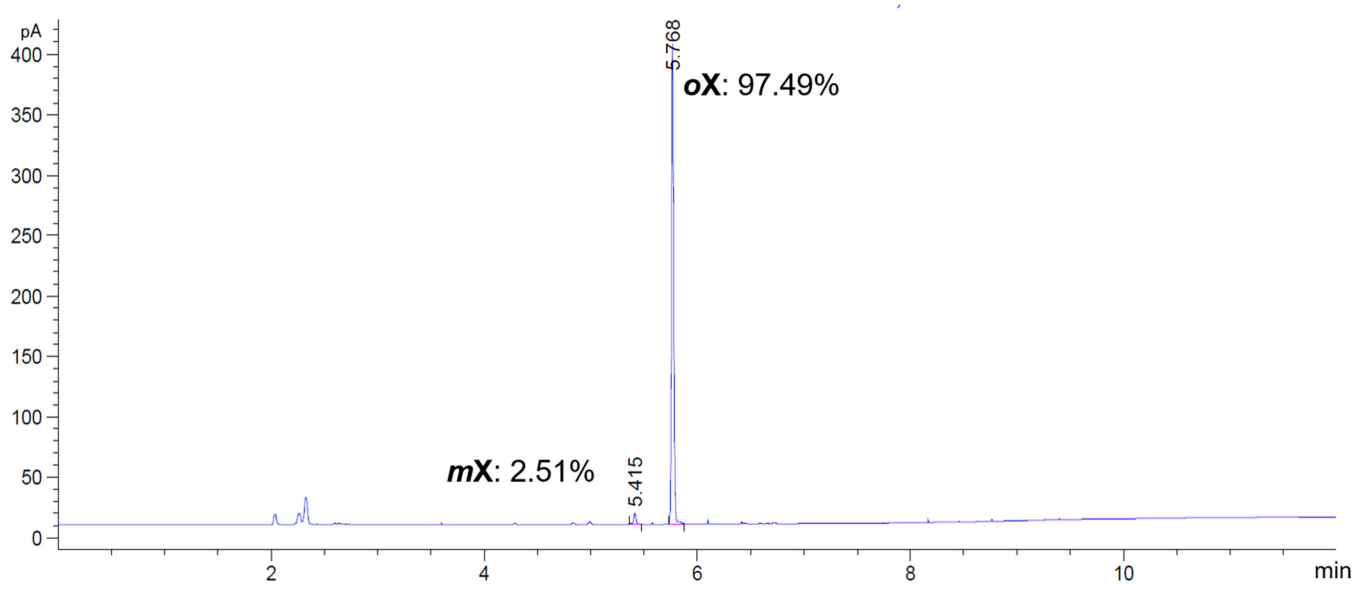


Fig. S23. Relative uptakes of ***o*X** and ***m*X** vapors adsorbed by **H*α*** for 12 h using head space gas chromatography.

An open 5 mL vial containing 2.00 mg of guest-free **H*α*** was placed in a sealed 20 mL vial containing 1 mL of the vapor mixture of ***o*X** and ***p*X** (*v*:*v* = 1:1). Uptake in **H*α*** was measured hour by hour by completely dissolving the crystals and measuring the ratio of ***o*X** or ***p*X** vapor to **H*α*** by ^{1}H NMR. The

relative uptakes of ***o*X** and ***p*X** vapors by **H*α*** were measured by heating the crystals to release the adsorbed vapor and detecting the relative amounts of ***o*X** and ***p*X** in the released vapor using head space gas chromatography.

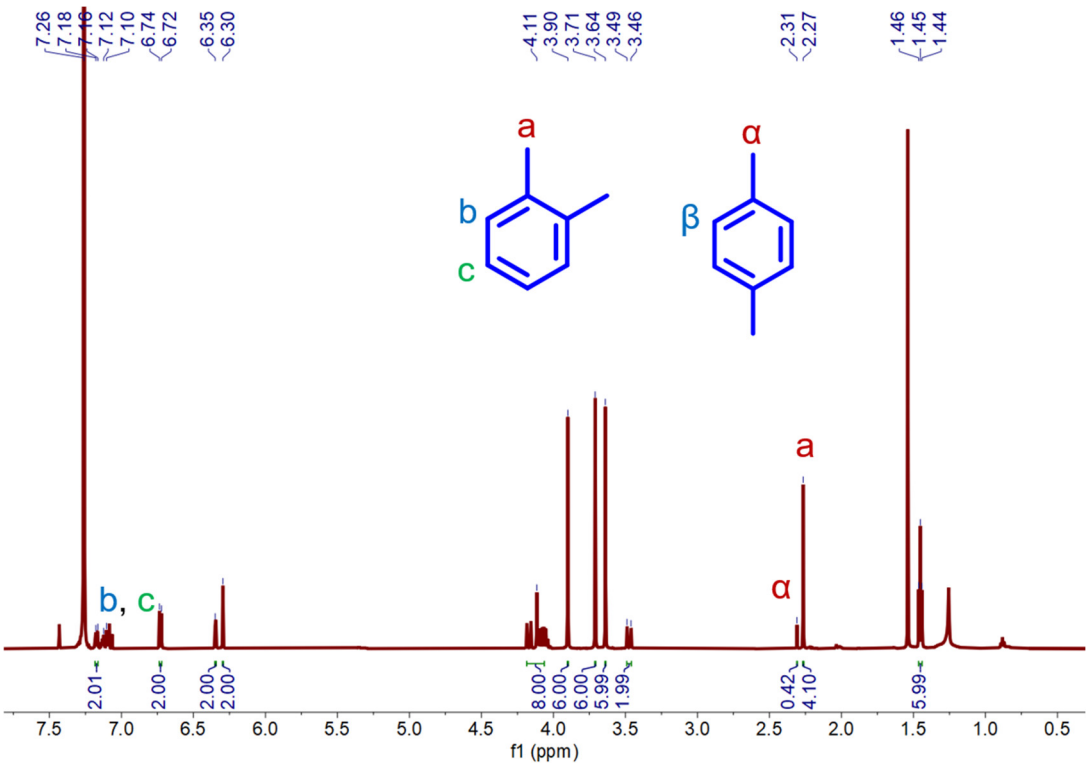


Fig. S24. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the mixture of ***o*X**/***p*X** (*v*:*v* = 1:1) for 12 h.

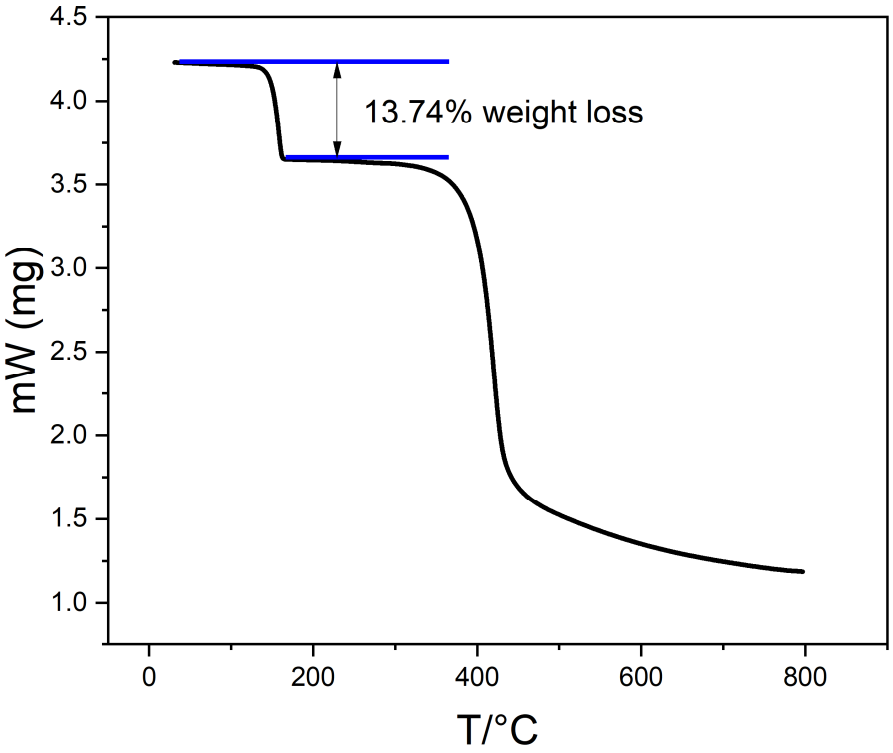


Fig. S25. Thermogravimetric analysis of **H*α*** after adsorption of the vapor mixture of ***o*X** and ***p*X** for 14 h. The weight loss below 200 °C can be calculated as 0.9 ***o*X** molecule per **H** molecule.

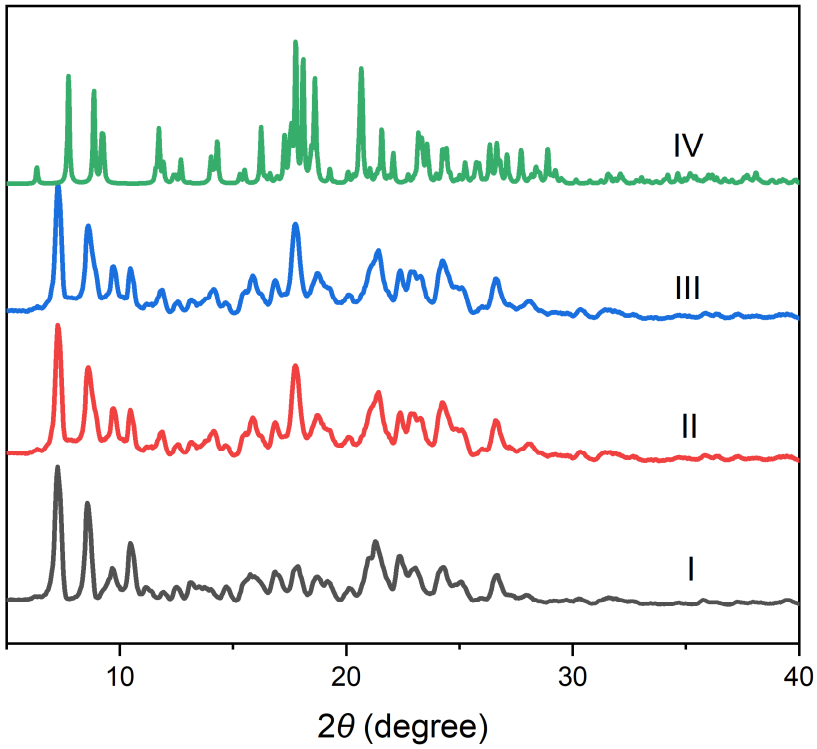


Fig. S26. PXRD patterns of **H*α***: (I) original **H*α***; (II) **H*α*** after adsorption of the mixture of ***o*X** and ***p*X**; (III) **H*α*** after adsorption of ***o*X**; (IV) simulated from single crystal of ***o*X@H**.

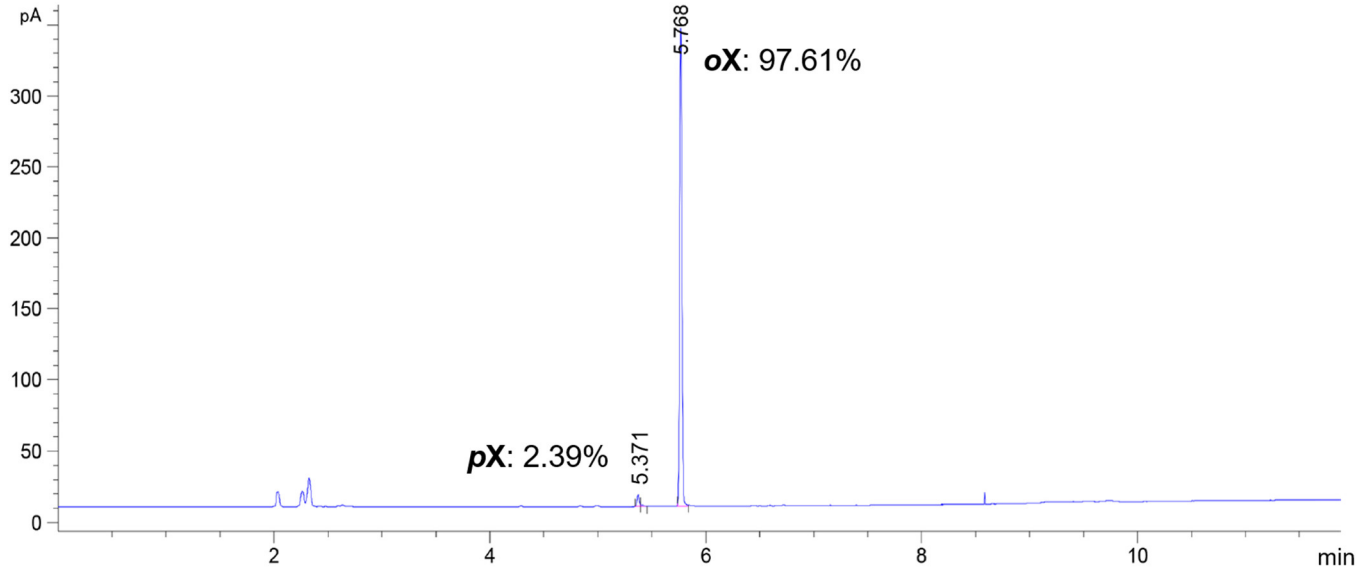


Fig. S27. Relative uptakes of ***o*X** and ***p*X** adsorbed in **H*α*** for 12 h using head space gas chromatography.

An open 5 mL vial containing 2.00 mg of guest-free **H*α*** was placed in a sealed 20 mL vial containing 1 mL of the vapor mixture of ***m*X** and ***p*X** (*v*:*v* = 1:1). Uptake in **H*α*** was measured hour by hour by completely dissolving the crystals and measuring the ratio of ***m*X** or ***p*X** to **H*α*** by ^{1}H NMR.

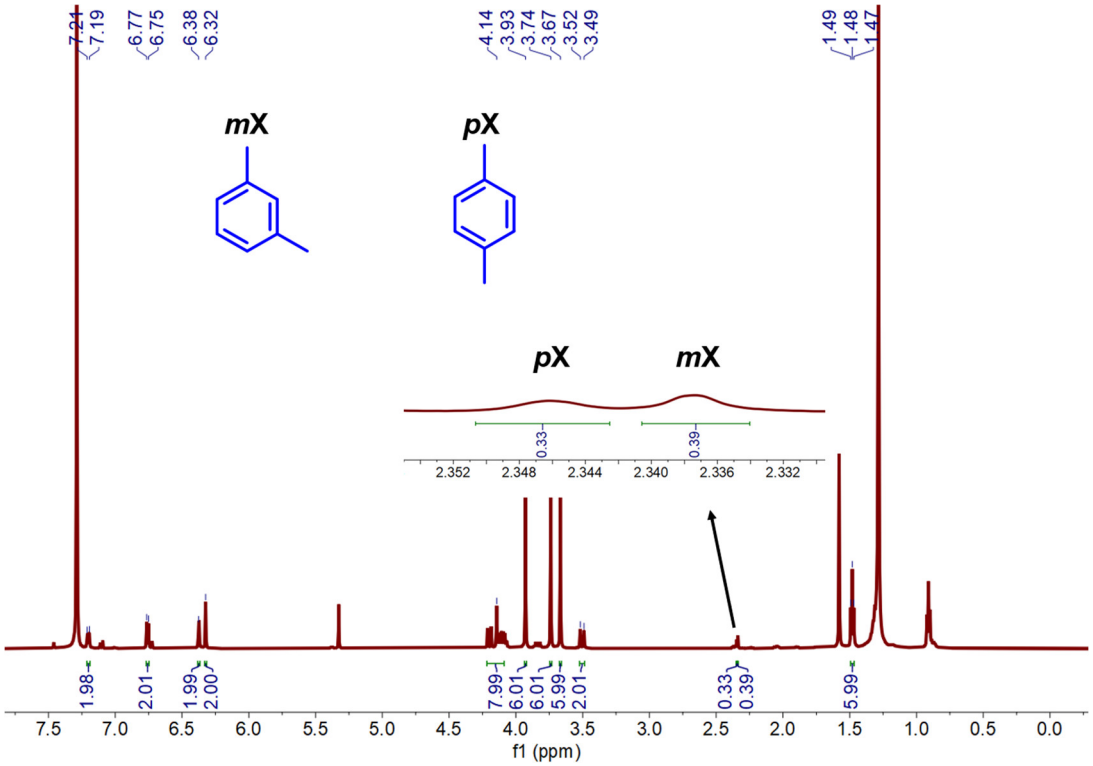


Fig. S28. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the vapor mixture of ***m*X** and ***p*X** (*v*:*v* = 1:1) for 12 h.

9. Uptake from the ternary mixture of xylene isomers by ***Hα***

An open 5 mL vial containing 2.00 mg of guest-free **H*α*** was placed in a sealed 20 mL vial containing 1 mL of the mixture of ***o*X/*p*X** (*v*:*v* = 1:1). Uptake in **H*α*** was measured hour by hour by completely dissolving the crystals and measuring the ratio of ***o*X** or ***p*X** to **H*α*** by ^{1}H NMR. The relative uptakes of ***o*X** and ***p*X** in **H*α*** were measured by heating the crystals to release the adsorbed vapor and detecting the relative amounts of ***o*X** and ***p*X** in the released vapor using head space gas chromatography.

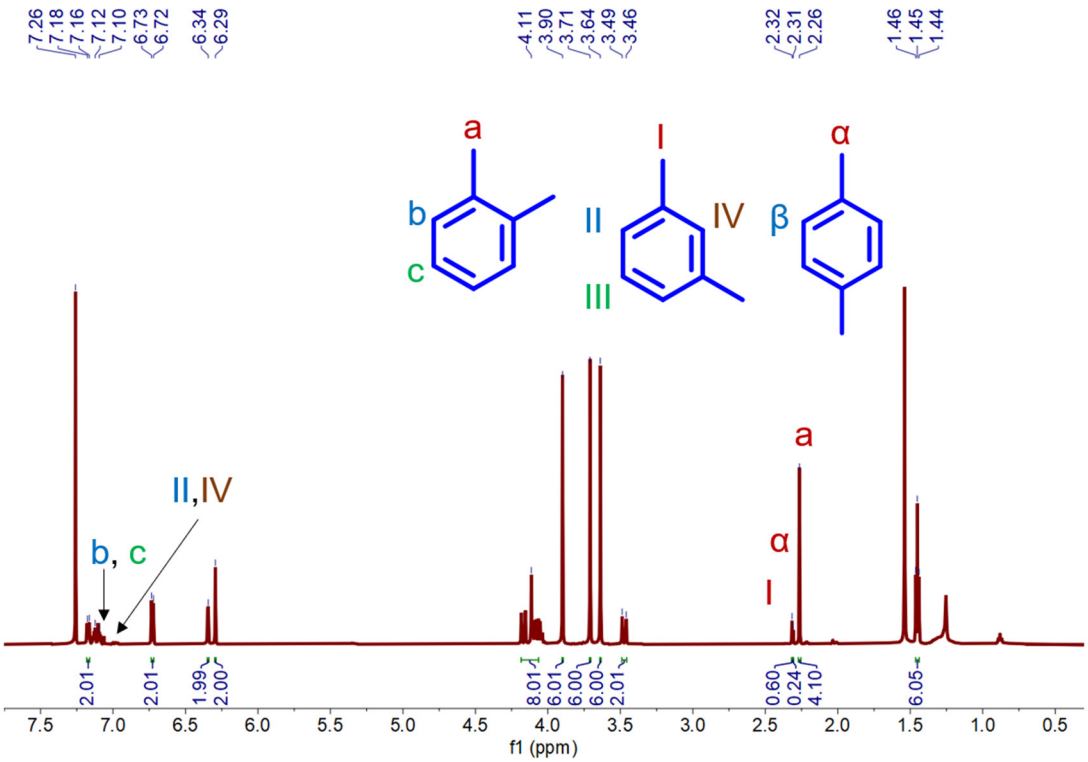


Fig. S29. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the ternary vapor mixture (***o*X**:***m*X**:***p*X**, *v*:*v*:*v* = 1:1:1) for 12 h.

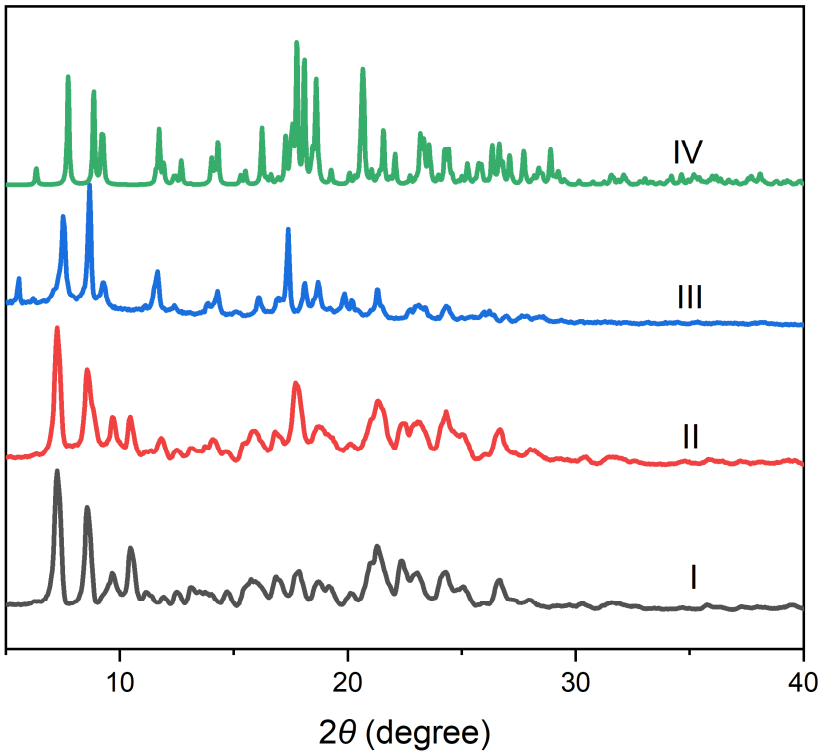


Fig. S30. PXRD patterns of **H*α***: (I) original **H*α***; (II) **H*α*** after adsorption of the ternary vapor mixture (***o*X**:***m*X**:***p*X**, *v*:*v*:*v* = 1:1:1); (III) **H*α*** after adsorption of ***o*X@H**; (IV) simulated from single crystal of ***o*X@H**.

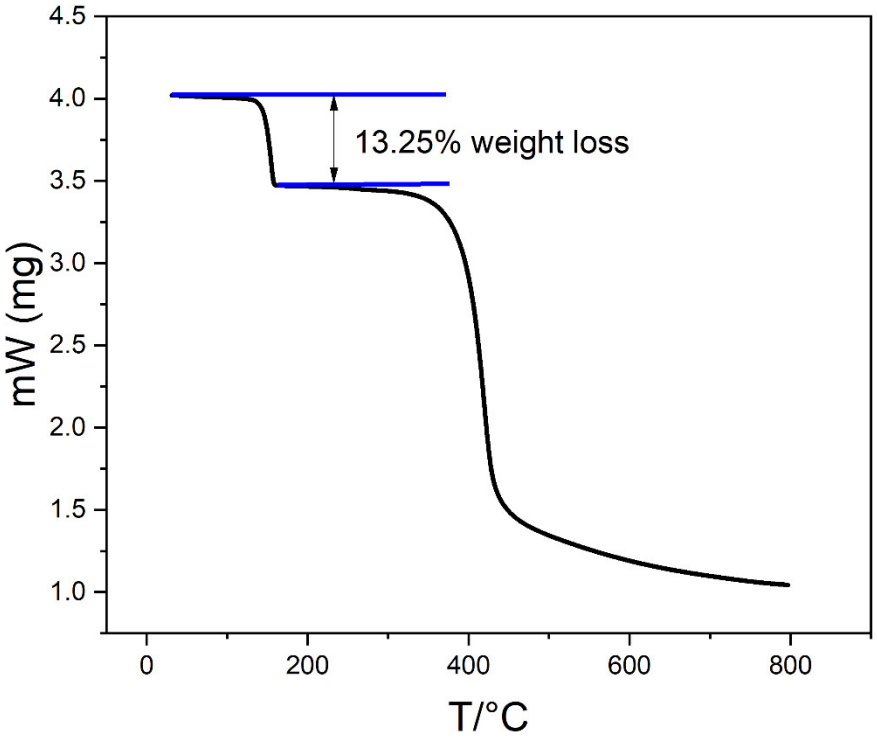


Fig. S31. Thermogravimetric analysis of **H** after adsorption of the ternary vapor mixture (***o*X**:***m*X**:***p*X**, *v*:*v*:*v* = 1:1:1) for 14 h. The weight loss below 200 °C can be calculated as 0.9 ***o*X** molecule per **H** molecule.

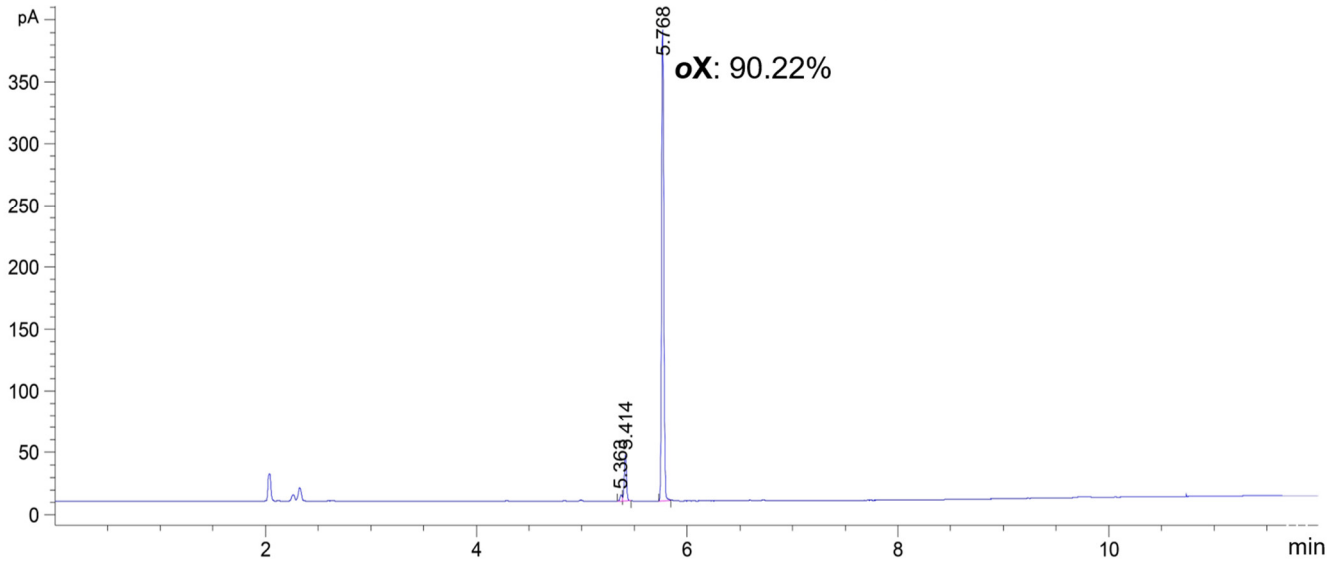


Fig. S32. Relative uptakes of ***o*X**, ***m*X** and ***p*X** vapors adsorbed by **H*α*** for 12 h using head space gas chromatography.

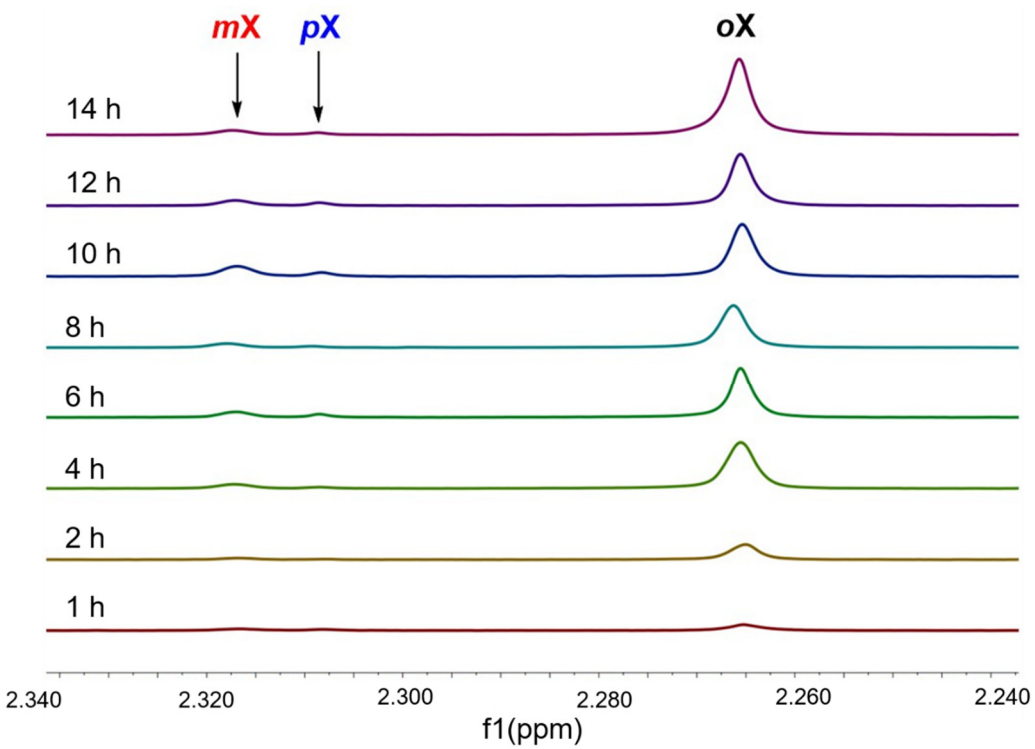


Fig. S33. Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the ternary vapor mixture (**oX**/***m*X**/***p*X**, *v*:*v*:*v* = 1:1:1) with different adsorption times.

10. Recyclability of ***Hα***

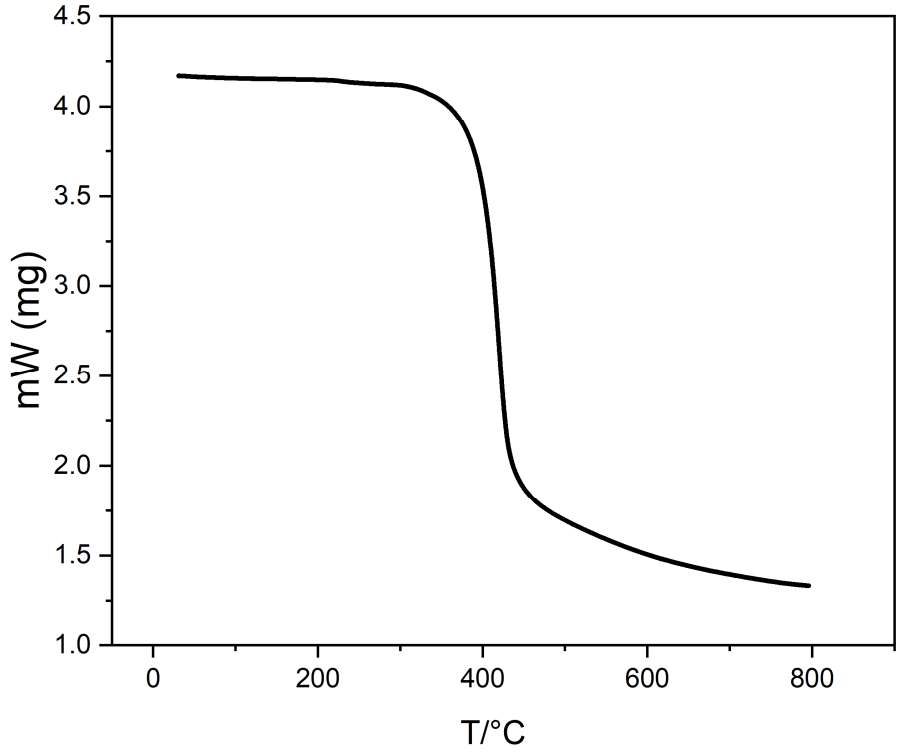


Fig. S34. Thermogravimetric analysis of ***o*X@H** using ethanol to disslove ***o*X**.

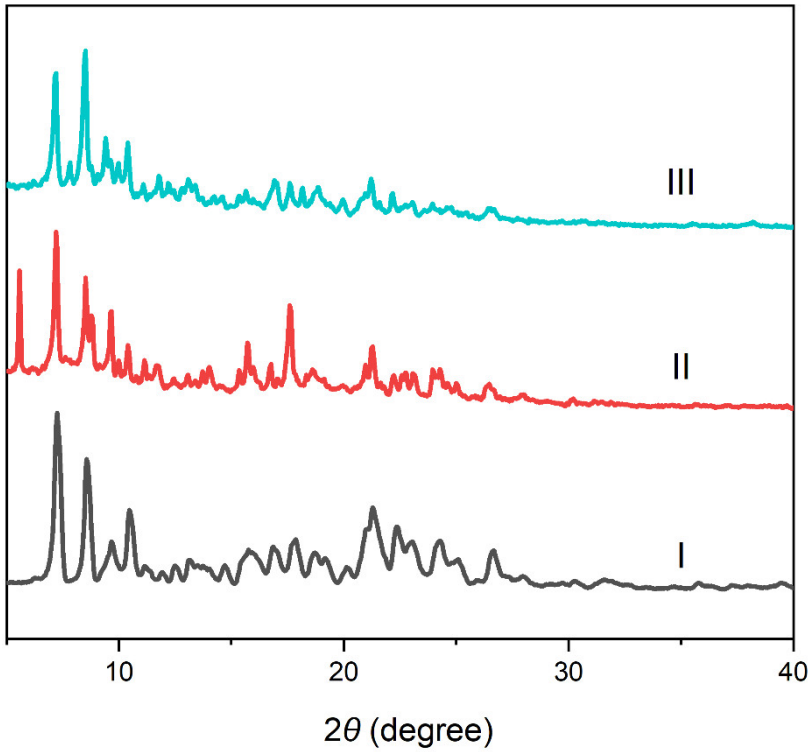


Fig. S35. PXRD patterns of: (I) original **Hα**; (II) **Hα** after adsorption of ***o*X** vapor; (III) **Hα** after 5 adsorption-desorption cycles.

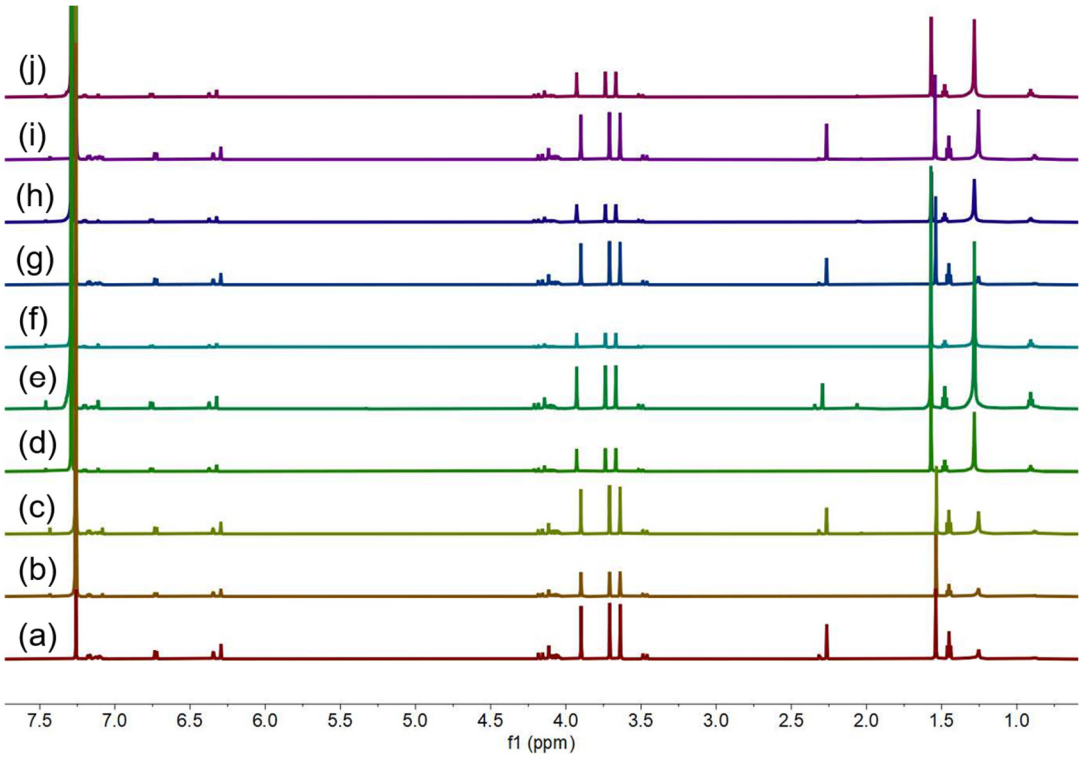


Fig. S36. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the ternary vapor mixture (**o*X*/*m*X/*p*X**, *v*:*v*:*v* = 1:1:1) for 5 cycles: (a) **H*α*** after adsorption of the ternary vapor mixture; (b) **H*α*** after desorption using ethanol to disslove ***o*X** for the first cycle; (c) **H*α*** after adsorption of the ternary vapor mixture for the second cycle; (d) **H*α*** after desorption using ethanol to disslove ***o*X** for the second cycle; (e) **H*α*** after adsorption of the ternary vapor mixture for the third cycle; (f) **H*α*** after desorption using ethanol to disslove ***o*X** for the third cycle; (g) **H*α*** after adsorption of the ternary vapor mixture for the fourth cycle; (h) **H*α*** after desorption using ethanol to disslove ***o*X** for the fourth cycle; (i) **H*α*** after adsorption of the ternary vapor mixture for the fifth cycle; (j) **H*α*** after desorption using ethanol to disslove ***o*X** for the fifth cycle.

11. Liquid-phase adsorption

11.1 Single-component adsorption for xylene isomers

In liquid−solid adsorption experiment of **H*α*** for single-component xylene isomers, 10.0 mg of **H*α*** was placed in a sealed 2 mL vial containing 1 mL of ***o*X**, ***m*X** or ***p*X** liquid, respectively. Time-dependent liquid–solid plots of **H*α*** were measured by completely dissolving the crystals and measuring the molar ratios of ***o*X**, ***m*X** and ***p*X** to **H*α*** by ^{1}H NMR and PXRD.

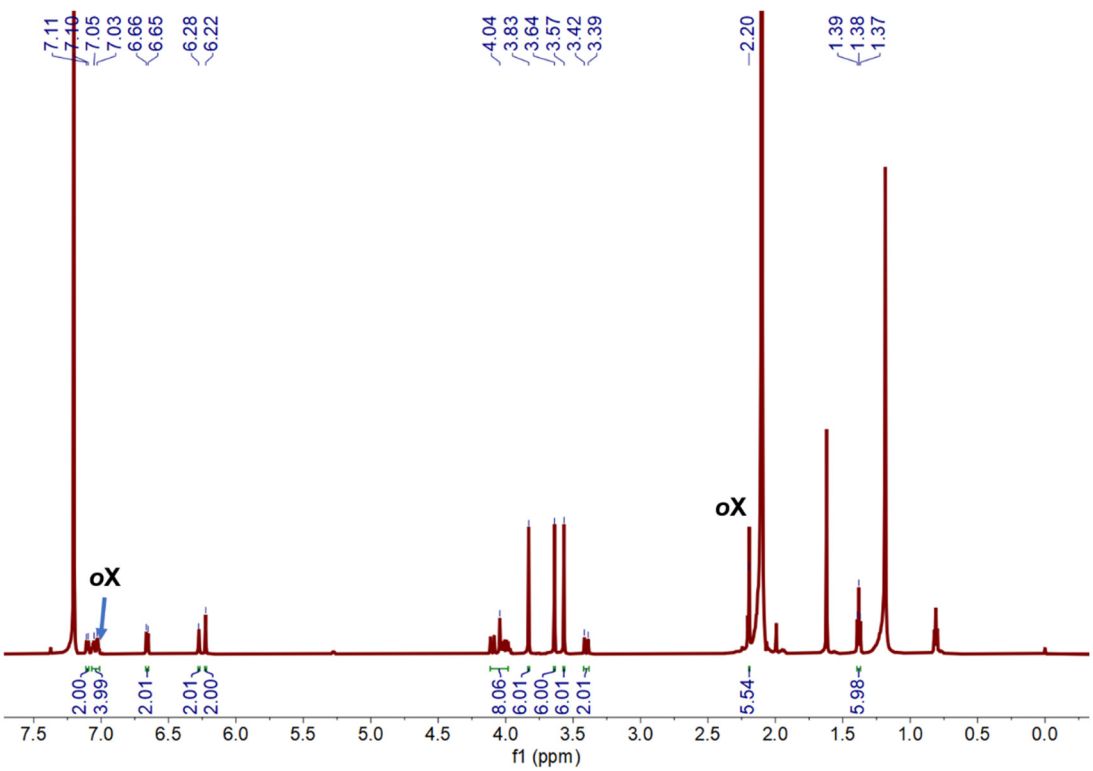


Fig. S37. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of ***o*X** liquid for 3 h.

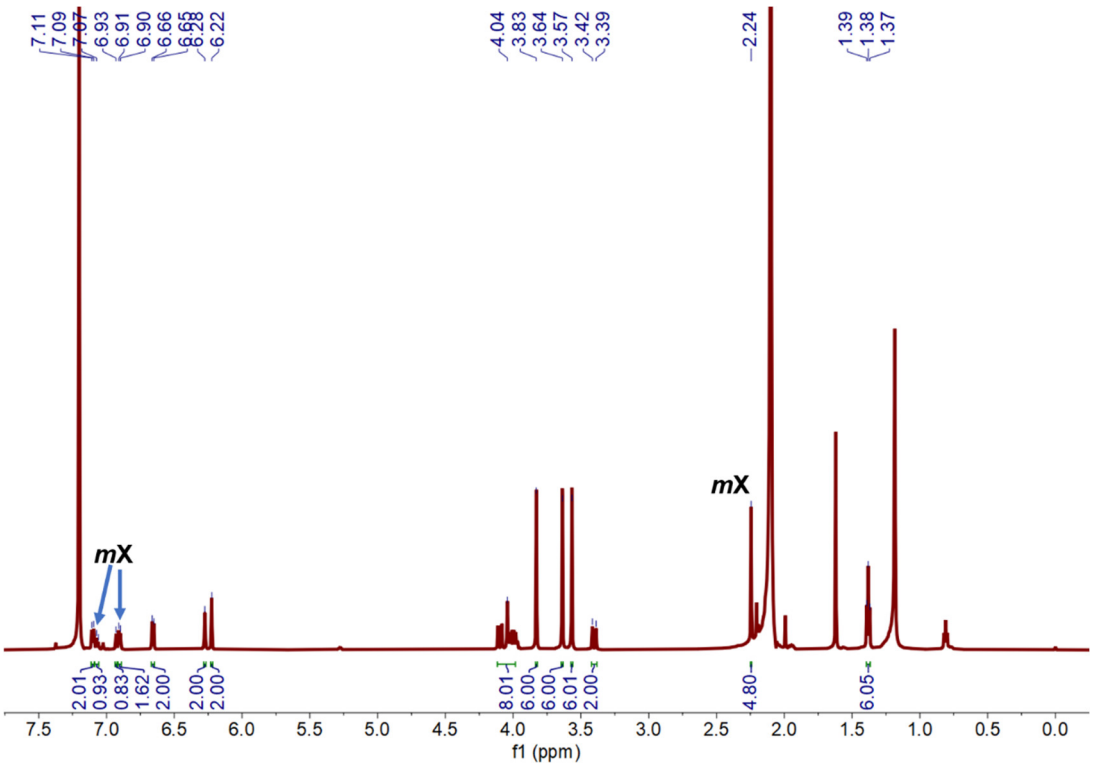


Fig. S38. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of ***m*X** liquid for 3 h.

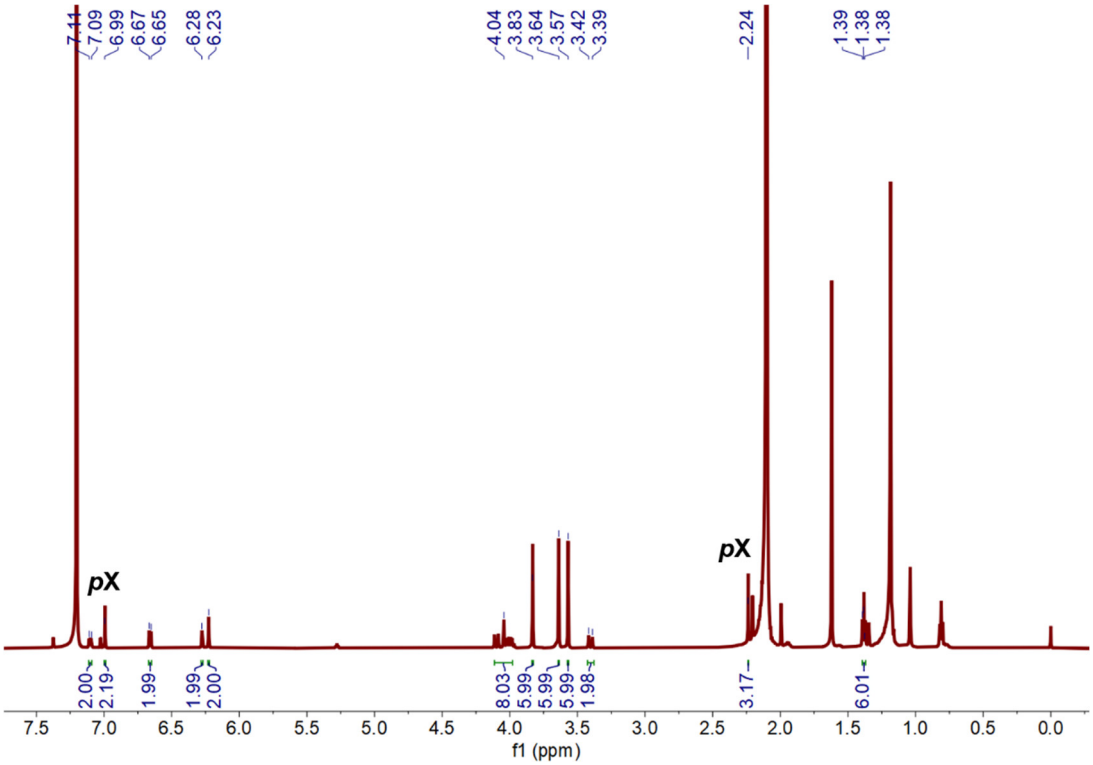


Fig. S39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of ***p*X** liquid for 3 h.

*11.2 Uptake from the ternary liquid mixture of xylene isomers in **Hα***

In liquid−solid adsorption experiment of **H*α*** for the ternary liquid mixture of xylene isomers, 10.0 mg of **H*α*** was placed in a sealed 2 mL vial containing 1 mL of the mixture of ***o*X**/***m*X**/***p*X** (*v*:*v*:*v* = 1:1:1). Time-dependent liquid–solid adsorption plots of **H*α*** were measured by completely dissolving the crystals and measuring the molar ratios of ***o*X**, ***m*X** and ***p*X** to **H*α*** by ^{1}H NMR, PXRD and GC experiments.

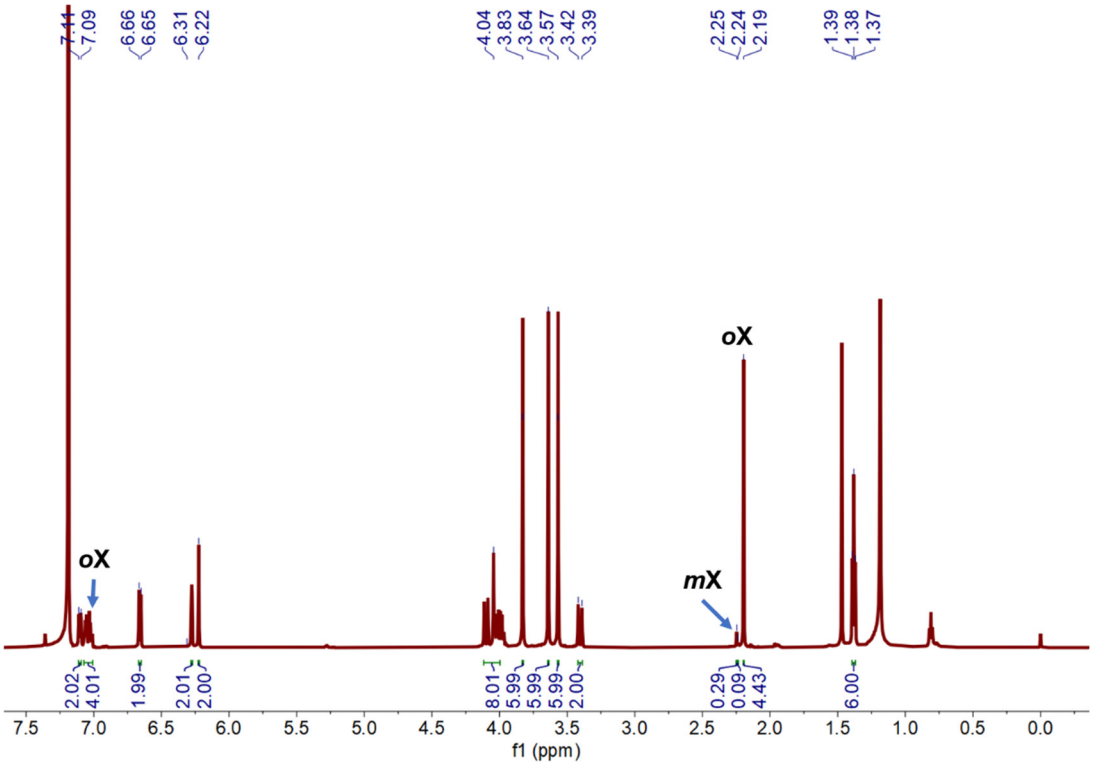


Fig. S40. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the ternary liquid mixture (***o*X**:***m*X**:***p*X**, *v*:*v*:*v* = 1:1:1) for 3 h.

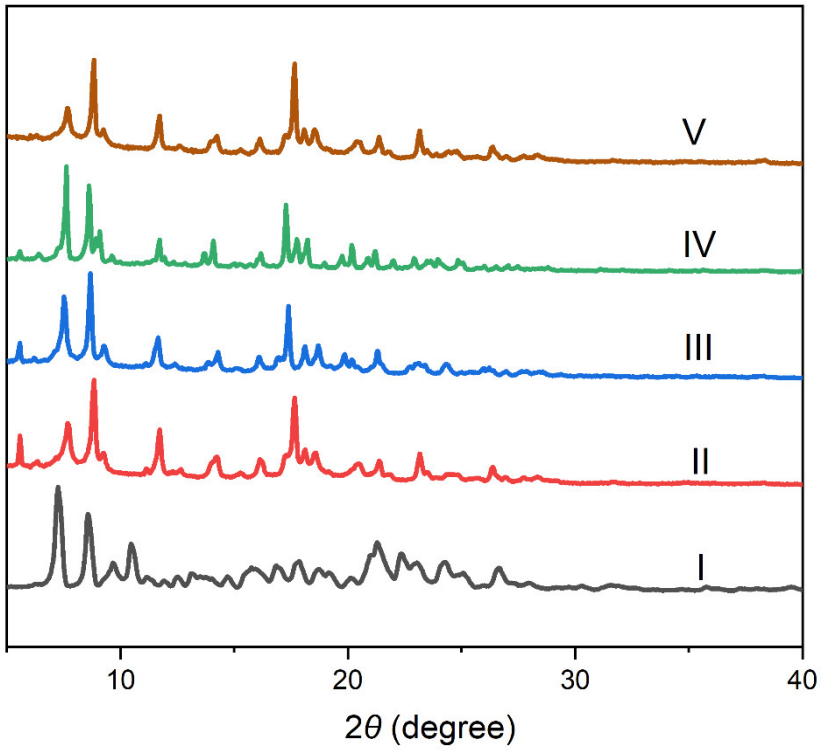


Fig. S41. PXRD patterns of: (I) original **H*α***; (II) **H*α*** after adsorbing ***o*X** liquid; (III) **H*α*** after adsorbing ***m*X** liquid; (IV) **H*α*** after adsorbing ***p*X** liquid; (V) **H*α*** after adsorbing the ternary liquid mixture (***o*X**/***m*X**/***p*X**, *v*:*v*:*v* = 1:1:1).

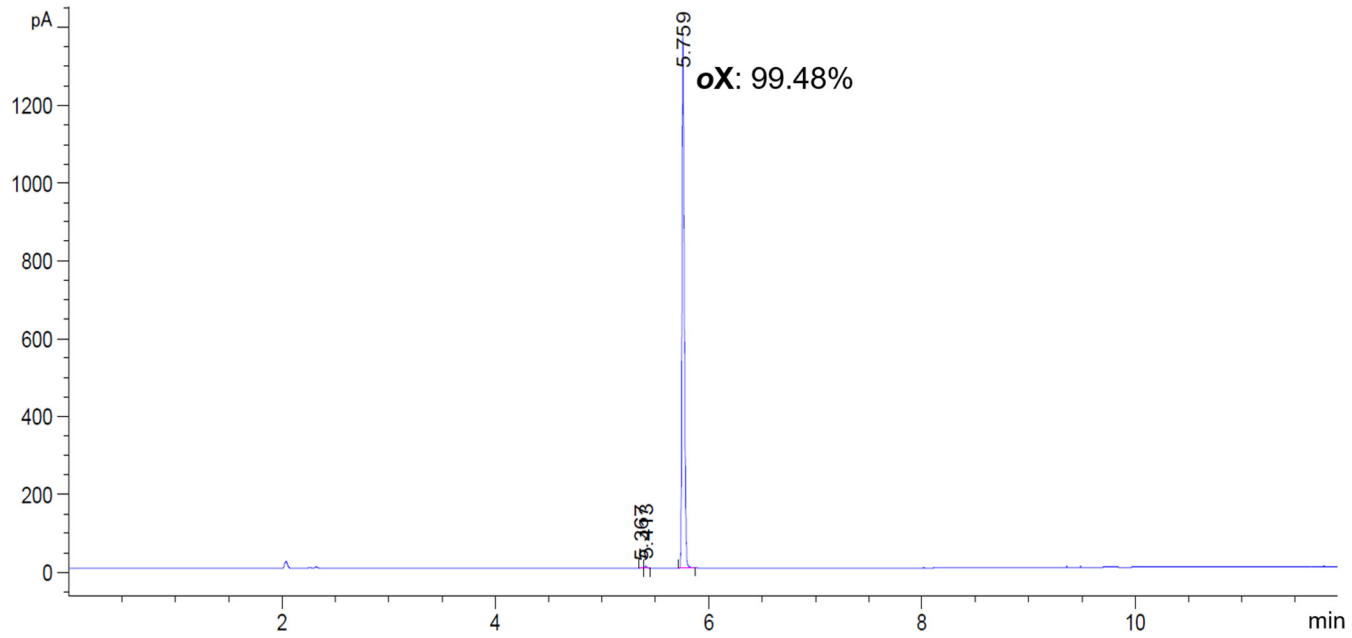


Fig. S42. Relative uptakes of ***o*X**, ***m*X** and ***p*X** liquids adsorbed by **H*α*** for 150 min using head space gas chromatography.

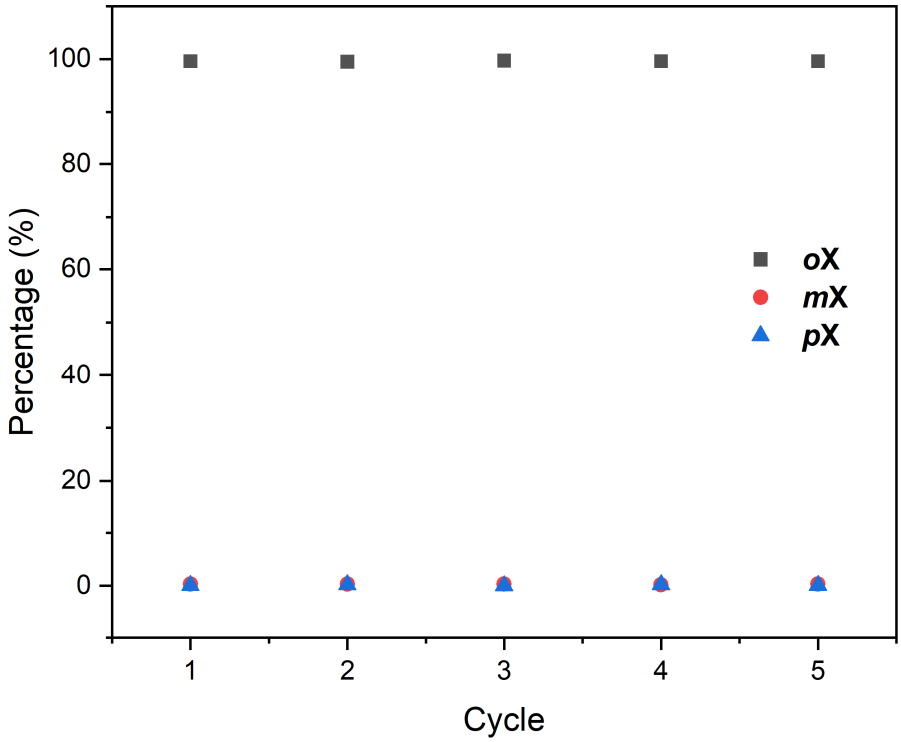


Fig. S43. Relative uptakes of ***o*X**, ***m*X** and ***p*X** liquids by **H*α*** after 5 cycles.

*12. Adsorption energies calculations of **Hα** for xylene isomers*

Table S4. Gibbs free energies of host, guest and host–guest complexes.

	△G (kJ/mol)
H*α*	-2036.95
***o*X**	-310.873
***m*X**	-310.870
***p*X**	-310.90
***o*X@H**	-2347.92
***m*X@H**	-2348.23
***p*X@H**	-2346.95

13. References

1. J. Zhou, J. Yang, B. Hua, L. Shao, Z. Zhang and G. Yu, The synthesis, structure, and molecular recognition properties of a [2]calix[1]biphenyl-type hybrid[3]arene. *Chem. Commun.*, 2016, **52**, 1622–1624.

2. J. Zhou, G. Yu, Q. Li, M. Wang and F. Huang, Separation of benzene and cyclohexane by nonporous adaptive crystals of a hybrid[3]arene. *J. Am. Chem. Soc.*, 2020, **142**, 2228–2232.