Highly Selective Separation of Toluene and Methylcyclohexane Based on Nonporous Adaptive Crystals of Hybrid[3]arene

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Electronic Supporting Information (18 pages)

1. Materials

All chemicals, including toluene (Tol) and methylcyclohexane (MCH), were purchased and used as received. Hybrid[3]arene **H** was synthesized as described previously.[S1] Activated crystalline **H** (**H*α***) was recrystallized from acetone and dried under vacuum at 120 °C overnight.

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 Cu Kα line (λ = 1.5418 Å). Data were measured over the range of 5−45° in 5°/min steps over 8 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

The single crystal of Tol@**H** was grown by slow evaporation: 2 mg of dry **H*α*** powders were put in a small vial where 2 mL of Tol was added. Then adding chloroform until all **H*α*** powers 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. Head Space 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 μm). Samples were analyzed using headspace injections and were performed by incubating the sample at 100 °C for 10 min, then sampling 1 mL of the headspace. The following HS-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) Calculation

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. Crystallography Data

Table S1. Experimental single crystal X-ray data for Tol@**H**.

Compound	Tol@**H**
Crystallization Solvent	Toluene
Collection Temperature [K]	300
Formula	$C_{81}H_{92}O_{16}$
Formula Weight	1321.54
Crystal System	Triclinic
Space Group	*P*-1
a [Å]	10.9484(18)
b [Å]	13.3498(18)
c [Å]	15.691(2)
α [°]	110.662(8)
β [°]	99.115(8)
γ [°]	107.401(8)
V [Å^3]	1956.1(5)
Z	1
D_{calcd} [Mg cm^{-3}]	1.122
Absorption coefficient [mm^{-1}]	0.624
F (000)	706
Crystal size [mm^3]	0.200 × 0.200 × 0.200
Theta range for data collection [°]	3.151 to 66.466
Index ranges	$-12 \le h \le 13$, $-15 \le k \le 15$, $-18 \le l \le 18$
Reflections collected	21988
Independent reflections	6812[R_{int} = 0.1237]
Data / restraints / parameters	6182 / 58 / 466
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.1297, wR_2 = 0.2953
R indices (all data)	R_1 = 0.2221, wR_2 = 0.3444
Goodness-of-fit on F^2	1.018
Largest diff. peak and hole [e.Å^{-3}]	0.529 and -0.340
CCDC	2304364

4. Characterization of Nonporous Adaptive Crystals of H (Hα)

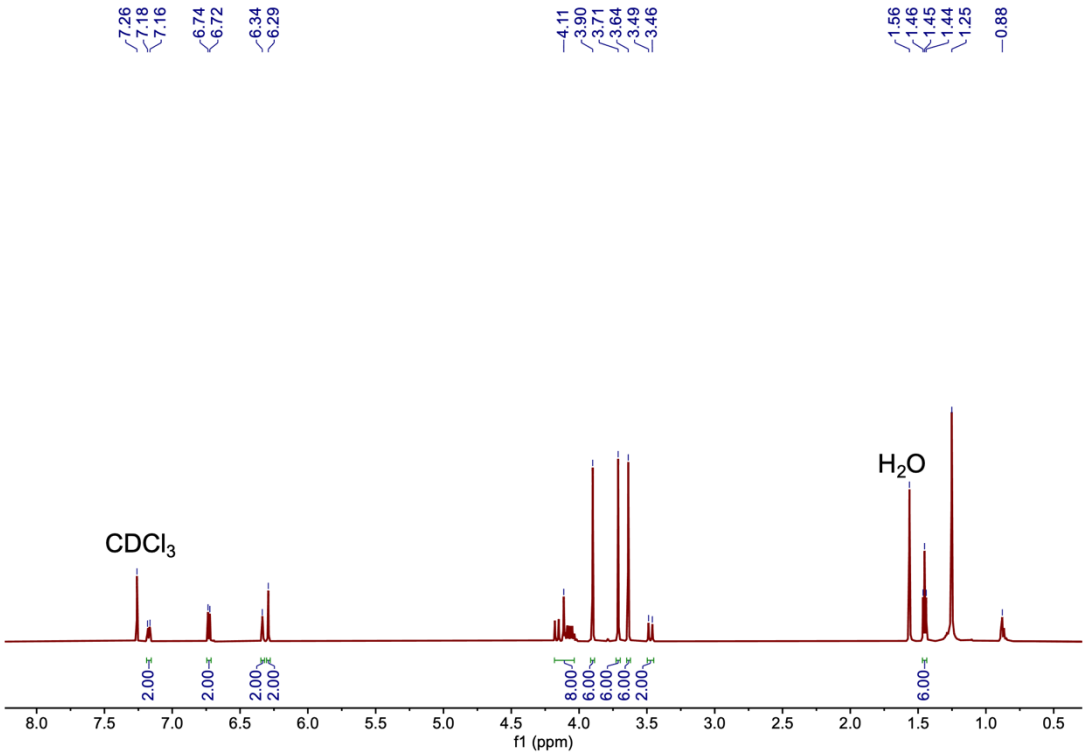

Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α***.

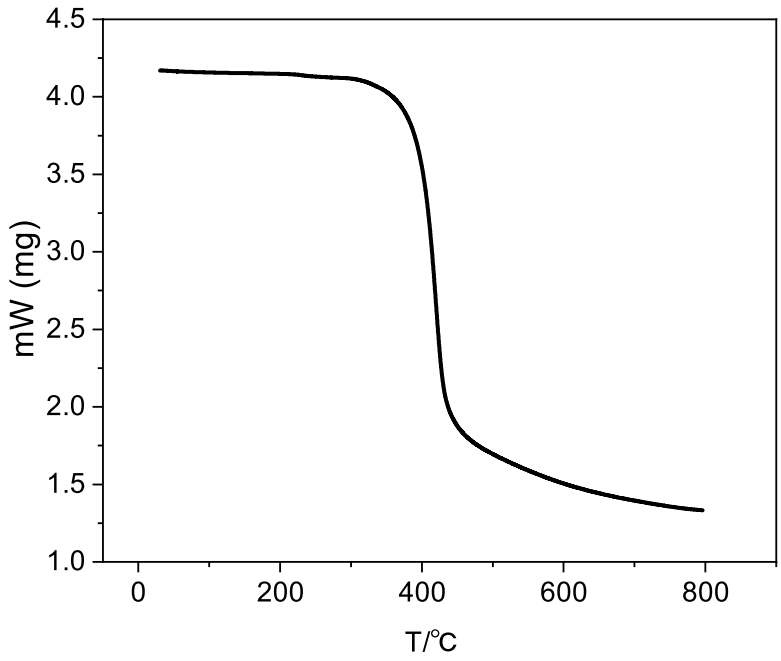

Figure S2. Thermogravimetric analysis of **H*α***.

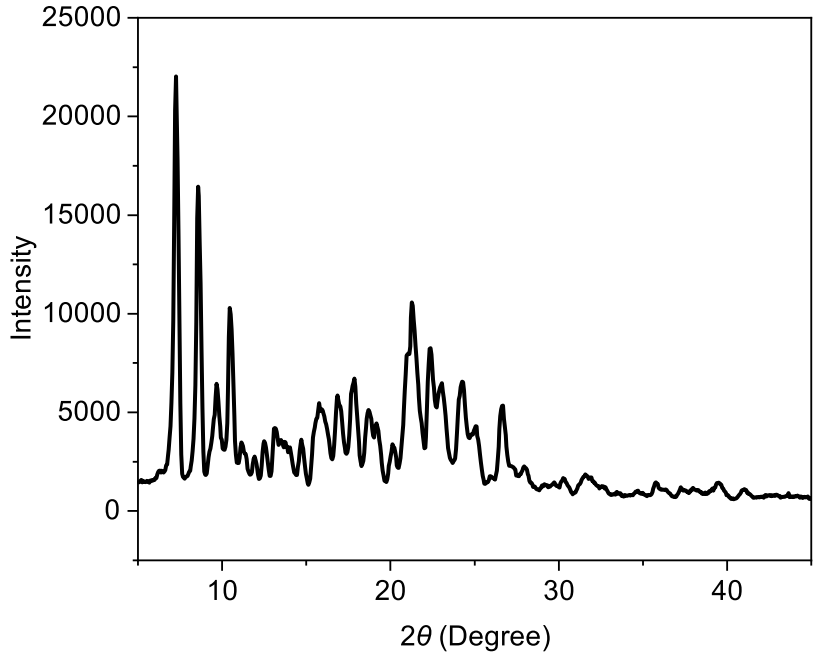

Figure S3. Powder X-ray diffraction pattern of **H*α***.

5. Single-Component Toluene and Methylcyclohexane Adsorption Experiments

An open 4 mL vial containing 1.00 mg of guest-free **H*α*** was placed in a sealed 20 mL vial containing 0.50 mL Tol or MCH. Uptake by **H*α*** was measured hour by hour by completely dissolving the crystals and measured the molecule ratios of Tol or MCH to **H*α*** by ^{1}H NMR. The results showed that the adsorption of Tol by **H*α*** could reach 0.8 mol/**H*α***. However, the adsorption of MCH by **H*α*** could be ignored. ^{1}H NMR experiments were performed by dissolving **H*α*** after vapor adsorption in $CDCl_3$. TGA profiles were recorded using **H*α*** after vapor adsorption.

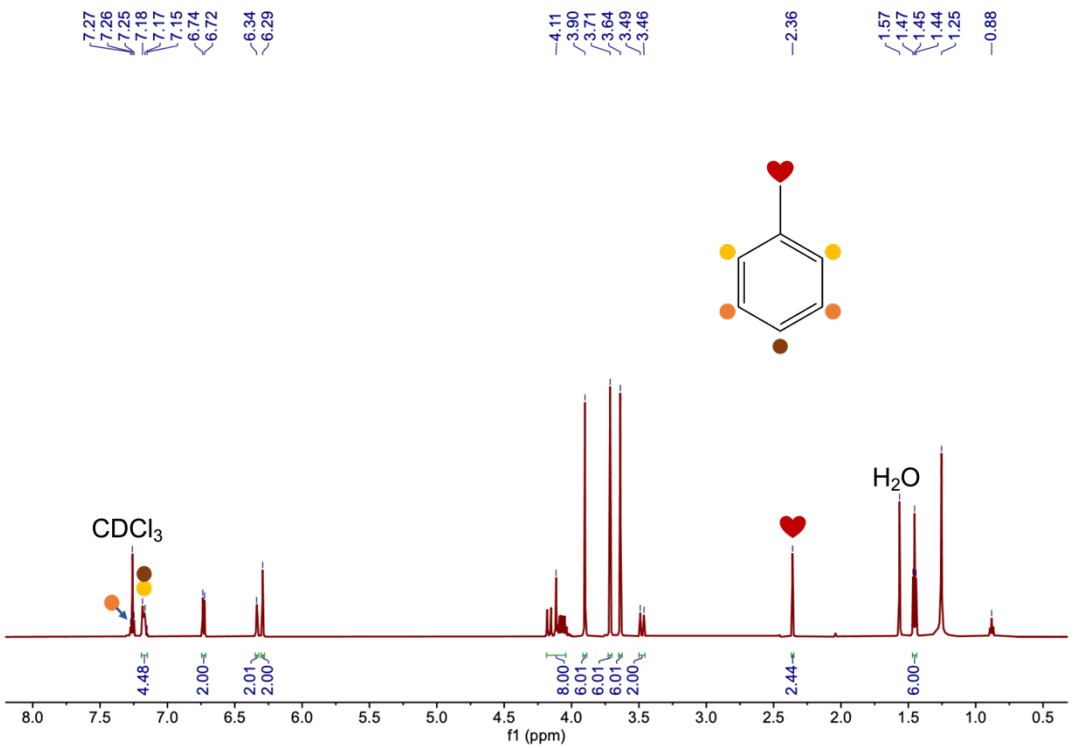

Figure S4. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of Tol vapor for 12 h.

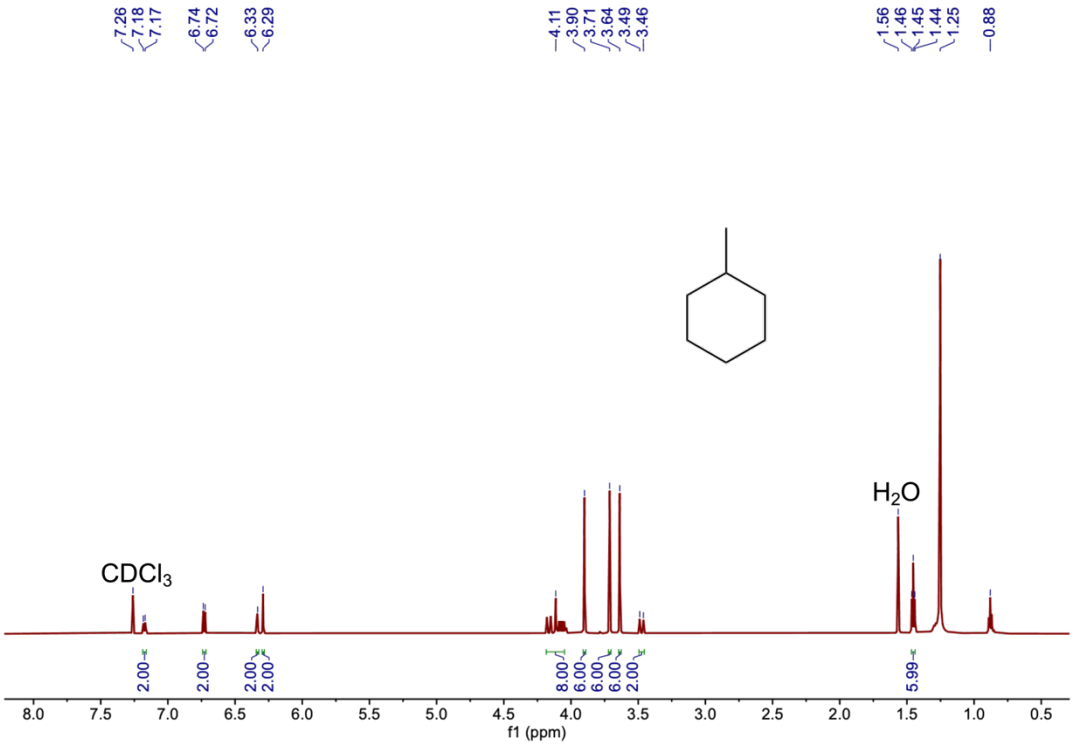

Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of MCH vapor for 12 h.

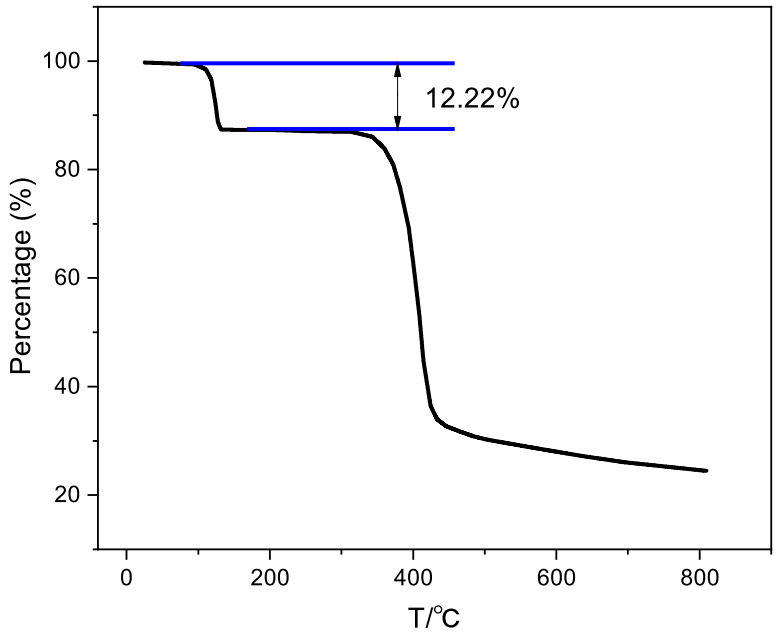

Figure S6. Thermogravimetric analysis of **H*α*** after adsorption of Tol vapor for 12 h. The weight loss below 150 °C can be calculated as 0.9 Tol molecule per **H*α*** molecule.

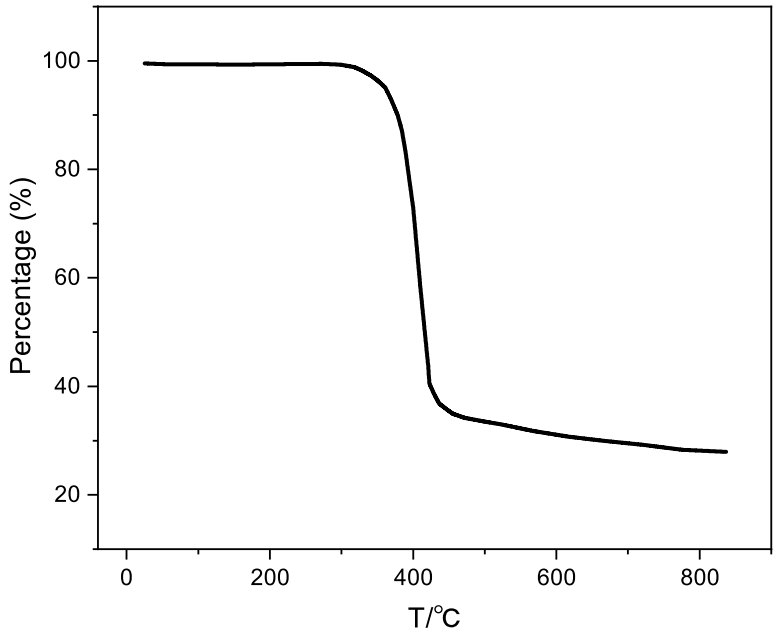

Figure S7. Thermogravimetric analysis of **H*α*** after adsorption of MCH vapor for 12 h.

6. Noncovalent Interactions Analysis in Single Crystal Structure of Tol@H

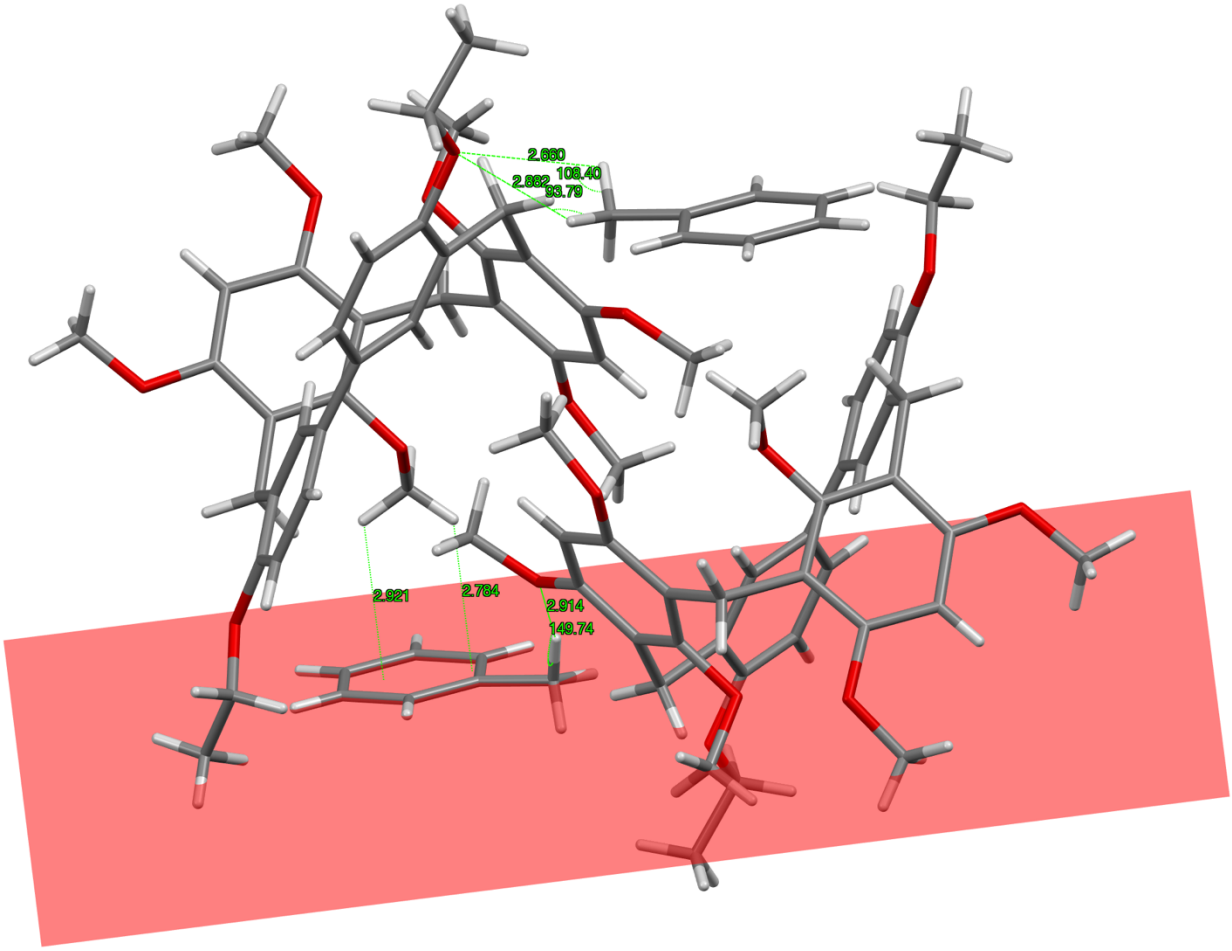

Figure S8. Illustration of C–H···π and C–H···O interactions between **H** and Tol. H–π-plane distances: 2.921 Å; 2.784 Å, H–O distances: 2.660 Å; 2.882 Å; 2.914 Å; angles: 108.40°; 93.79°; 149.74°.

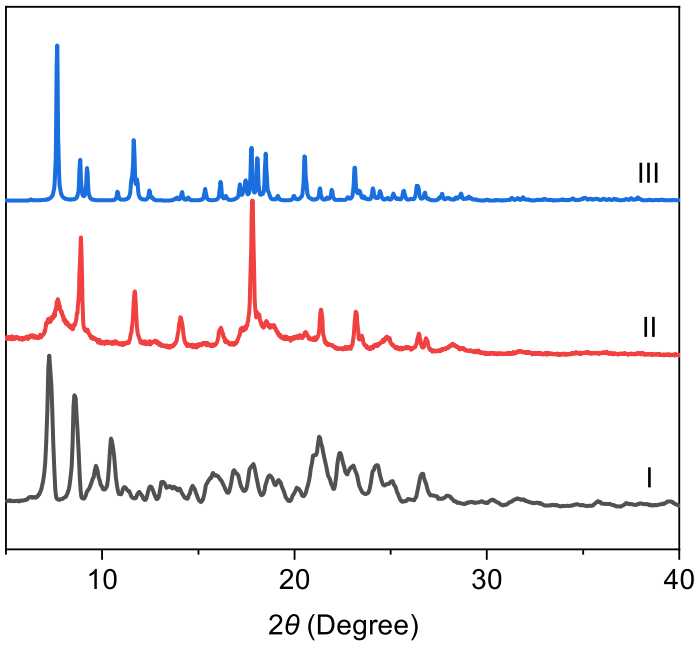

Figure S9. PXRD patterns of: (I) original **H*α***; (II) **H*α*** after adsorption of Tol vapor; (III) simulated from the single crystal structure of Tol@**H**.

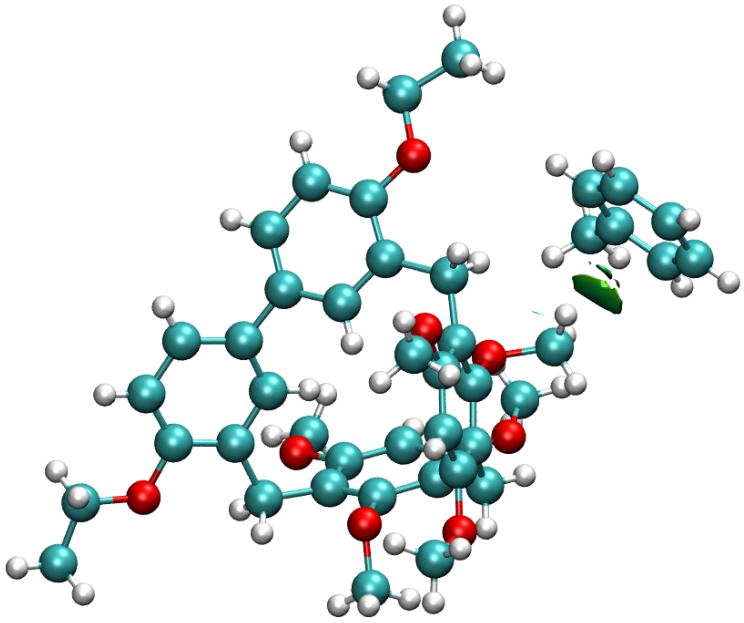

Figure S10. Visual study of weak intermolecular interactions of Tol@**H** by DFT calculation.

7. Uptake from the Mixture of Toluene and Methylcyclohexane by Hα

An open 4 mL vial containing 1.00 mg of guest-free **Hα** was placed in a sealed 20 mL vial containing Tol and MCH (0.5 mL:0.5 mL). Uptake by **Hα** was measured hour by hour by completely dissolving the crystals and measured the molecule ratios of Tol and MCH to **Hα** by ^{1}H NMR. **Hα** could selectively adsorb Tol but hardly adsorb MCH. The adsorption of Tol could reach 0.80 mol/**Hα**.

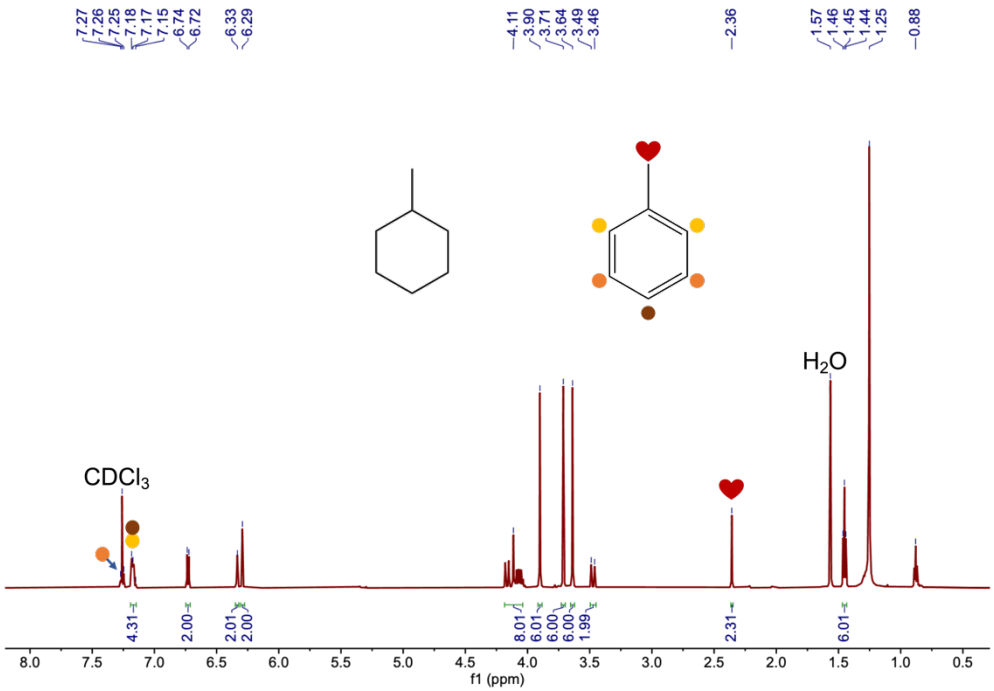

Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **Hα** after adsorption of the vapor mixture of Tol and MCH (*v*:*v* = 1:1) for 24 h.

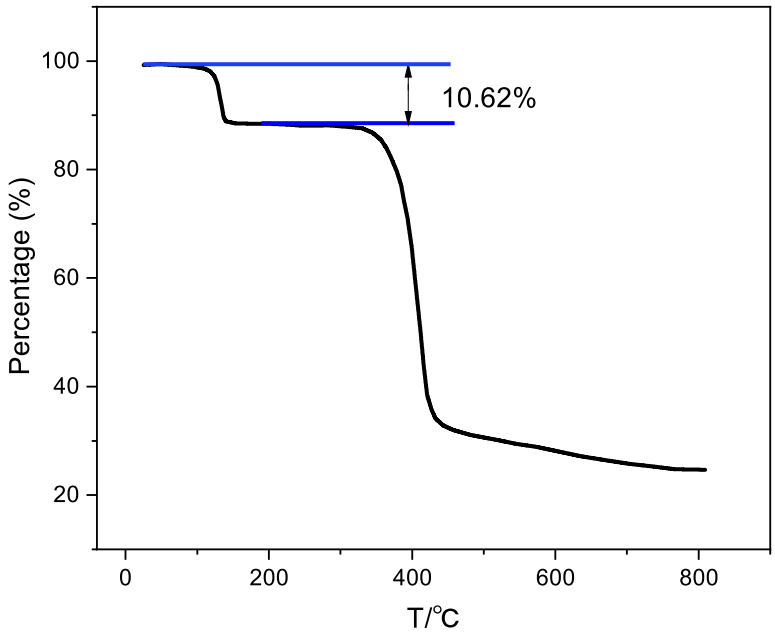

Figure S12. Thermogravimetric analysis of **H*α*** after adsorption of the vapor mixture of Tol and MCH (*v*:*v* = 1:1) for 24 h. The weight loss below 150 °C can be calculated as 0.8 Tol molecule per **H*α*** molecule.

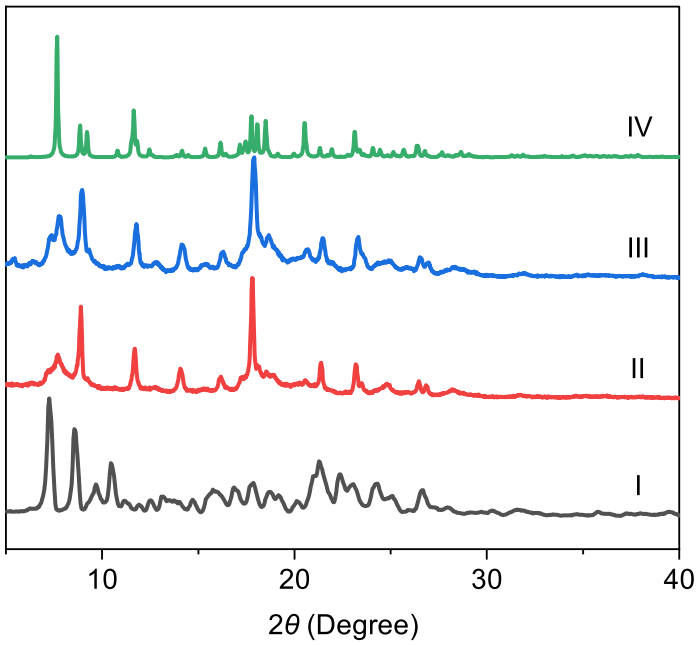

Figure S13. PXRD patterns of: (I) original **H*α***; (II) **H*α*** after adsorption of Tol vapor; (III) **H*α*** after adsorption of the vapor mixture of Tol and MCH (*v*:*v* = 1:1); (IV) simulated from the single crystal structure of Tol@**H**.

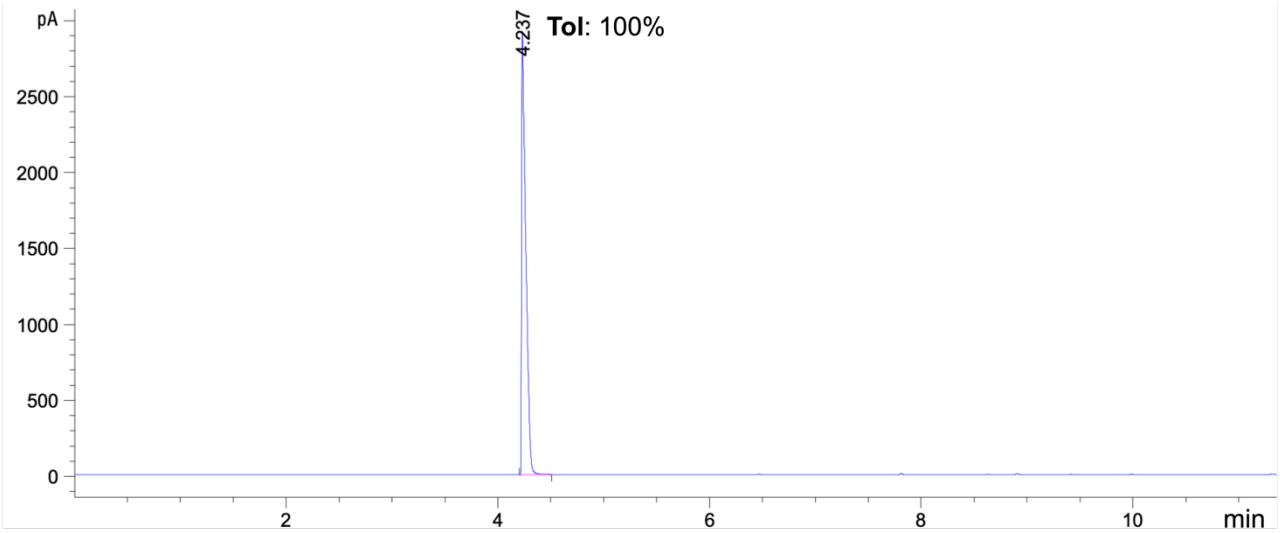

Figure S14. Relative uptakes of Tol and MCH vapors adsorbed by **H*α*** for 24 h using head space gas chromatography.

8. Recyclability of Hα

An open 5 mL vial containing 20.0 mg of Tol@**H** was desolvated by heating under vacuum at 120 °C overnight. The resultant crystals were characterized by PXRD, ^{1}H NMR and head space gas chromatography experiments.

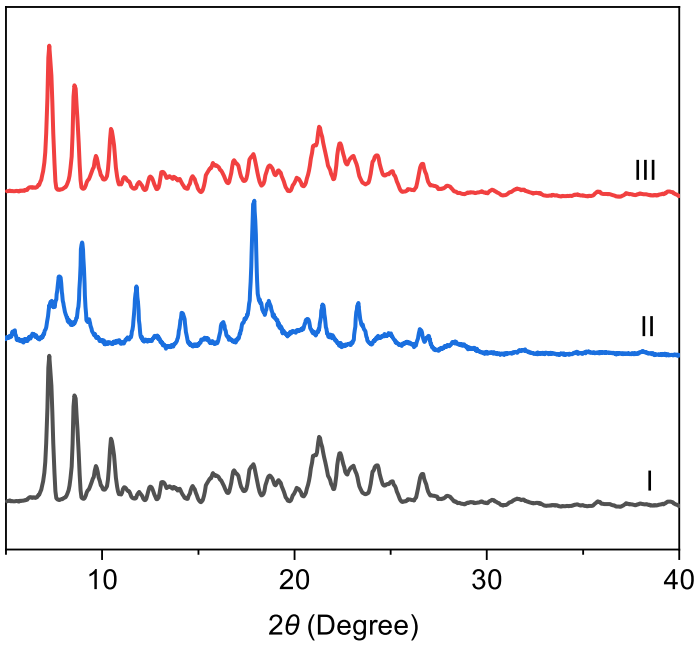

Figure S15. PXRD patterns of: (I) original **H*α***; (II) **H*α*** after adsorption of the vapor mixture of Tol and MCH (*v*:*v* = 1:1); (III) **H*α*** after 5 adsorption-desorption cycles.

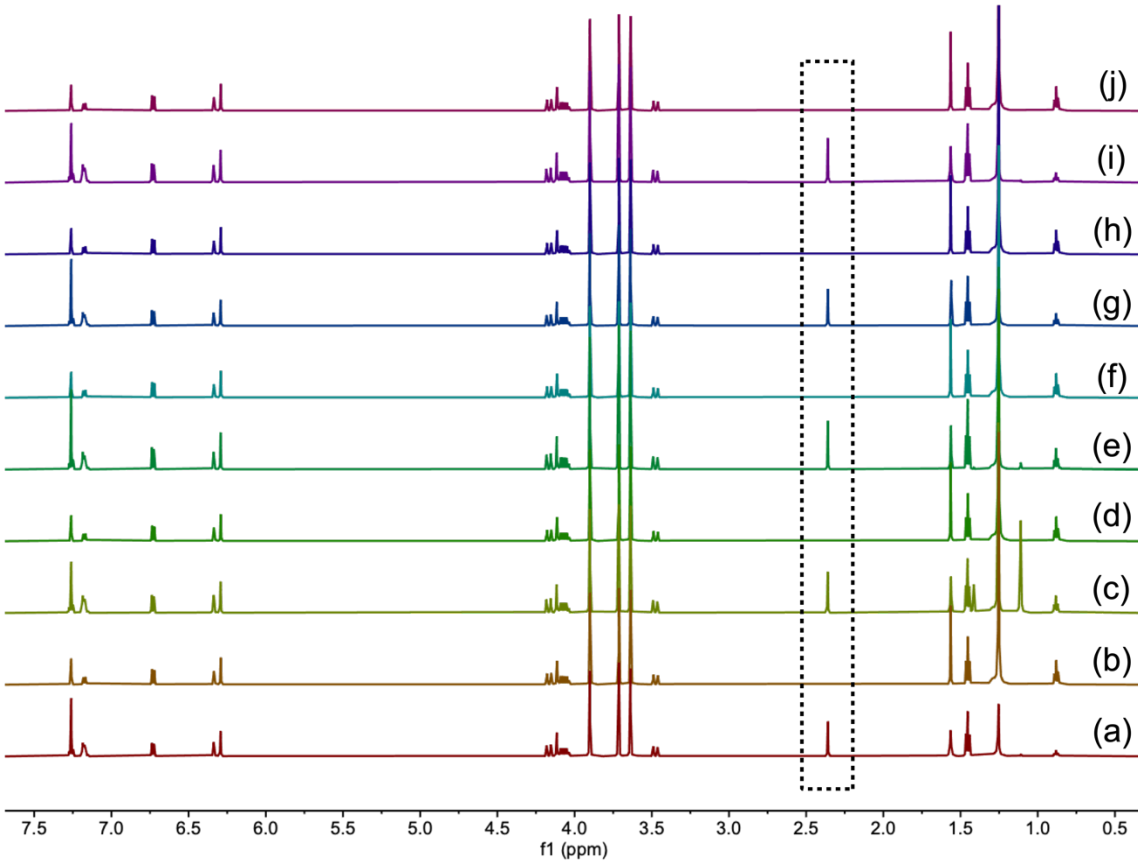

Figure S16. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the vapor mixture of Tol and MCH (*v*:*v*: = 1:1) for 5 cycles: (a) **H*α*** after adsorption of the vapor mixture of Tol and MCH for the first cycle; (b) **H*α*** after desorption of Tol for the first cycle; (c) **H*α*** after adsorption of the vapor mixture of Tol and MCH for the second cycle; (d) **H*α*** after desorption of Tol for the second cycle; (e) **H*α*** after adsorption of the vapor mixture of Tol and MCH for the third cycle; (f) **H*α*** after desorption of Tol for the third cycle; (g) **H*α*** after adsorption of the vapor mixture of Tol and MCH for the fourth cycle; (h) **H*α*** after desorption of Tol for the fourth cycle; (i) **H*α*** after adsorption of the vapor mixture of Tol and MCH for the fifth cycle; (j) **H*α*** after desorption of Tol for the fifth cycle.

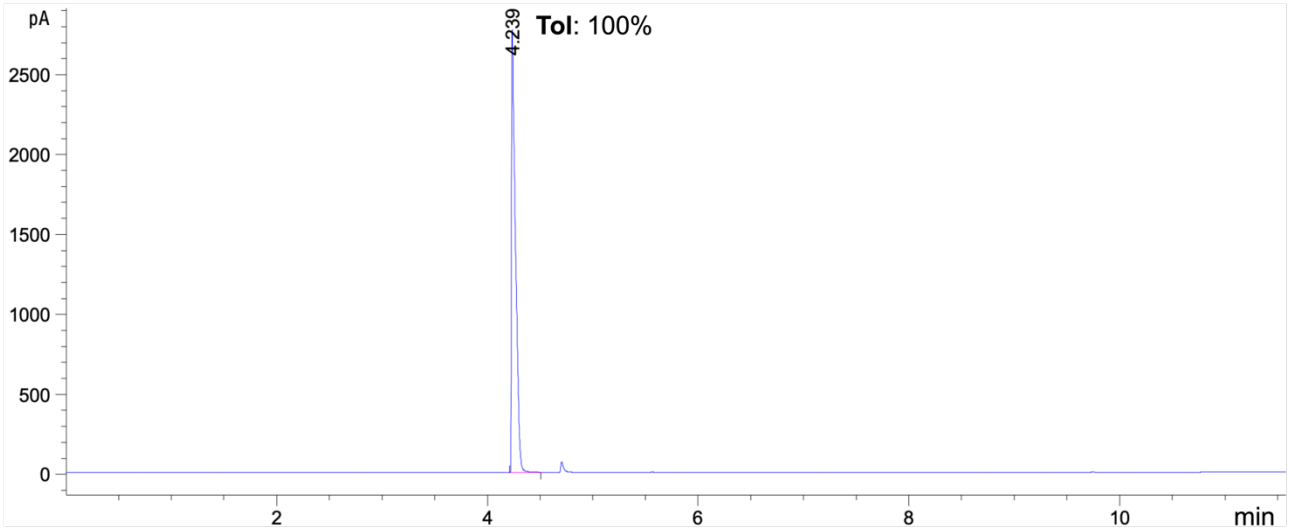

Figure S17. Relative uptakes of Tol and MCH vapors adsorbed by **H*α*** after 5 cycles using head space gas chromatography.

9. Liquid-Solid Adsorption

9.1 Single-component Adsorption for Toluene and Methylcyclohexane

For each liquid-solid adsorption experiment, 10.0 mg of **H*α*** were placed in a sealed 2 mL vial containing 1 mL of Tol or MCH liquid. Time-dependent liquid-solid plots of **H*α*** were measured by completely dissolving the crystals and measuring the molecule ratios of Tol and MCH to **H*α*** by ^{1}H NMR.

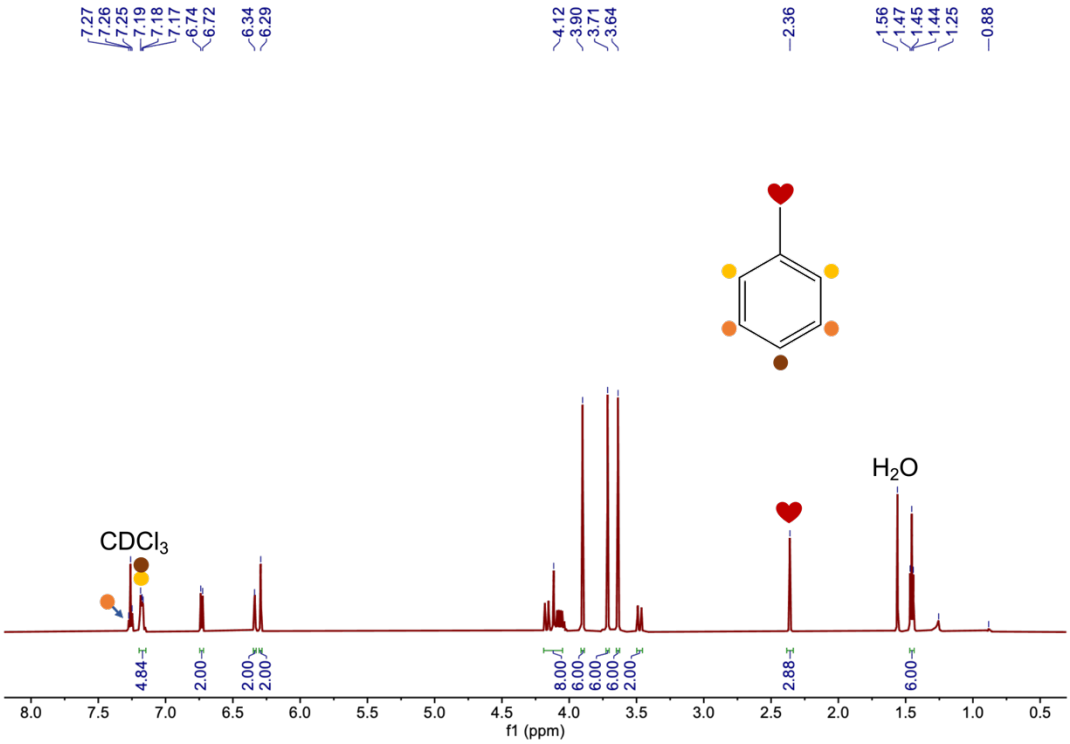

Figure S18. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of Tol liquid for 60 min.

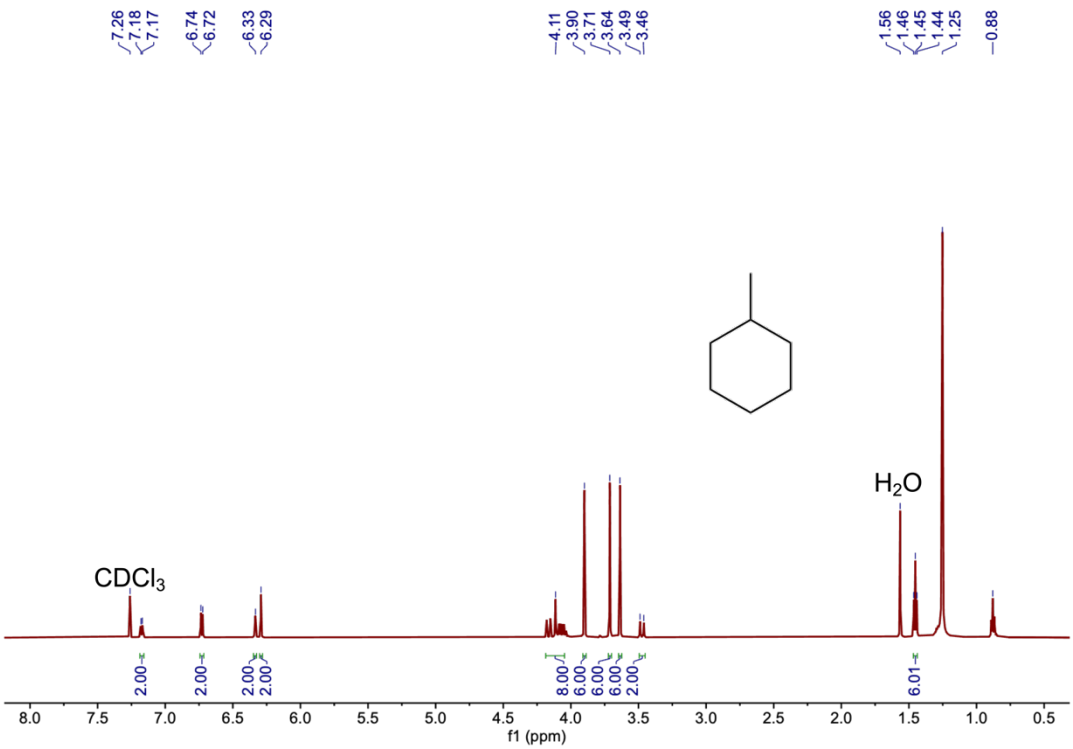

Figure S19. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of MCH liquid for 60 min.

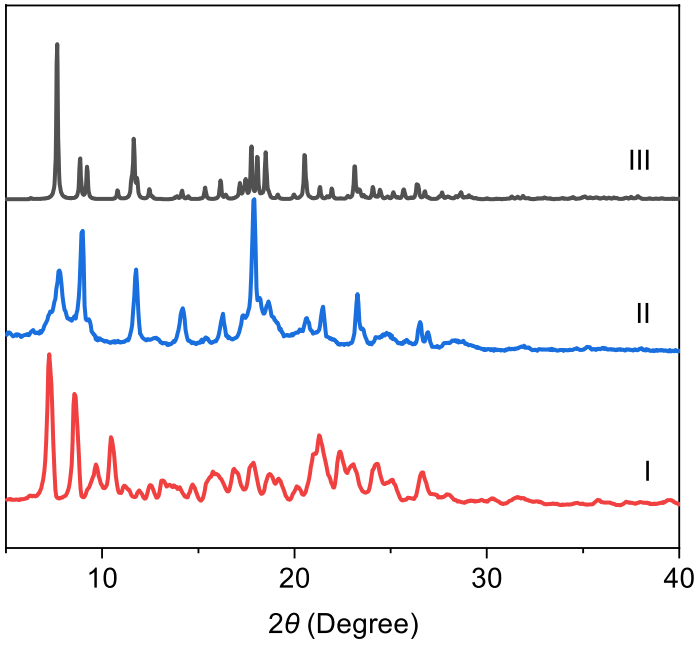

Figure S20. PXRD patterns of: (I) original **H*α***; (II) **H*α*** after adsorption of the Tol liquid; (III) simulated from the single crystal structure of Tol@**H**.

9.2 Adsorption for the Mixture of Toluene and Methylcyclohexane

For each liquid-solid adsorption experiment, 10.0 mg of **H*α*** were placed in a sealed 2 mL vial containing 1 mL of the mixture of Tol and MCH (0.5 mL:0.5 mL). Time-dependent **H*α*** liquid-solid adsorption plots were measured by completely dissolving the crystals and measuring the molecule ratios of Tol and MCH to **H*α*** by ^{1}H NMR and head space gas chromatography experiments.

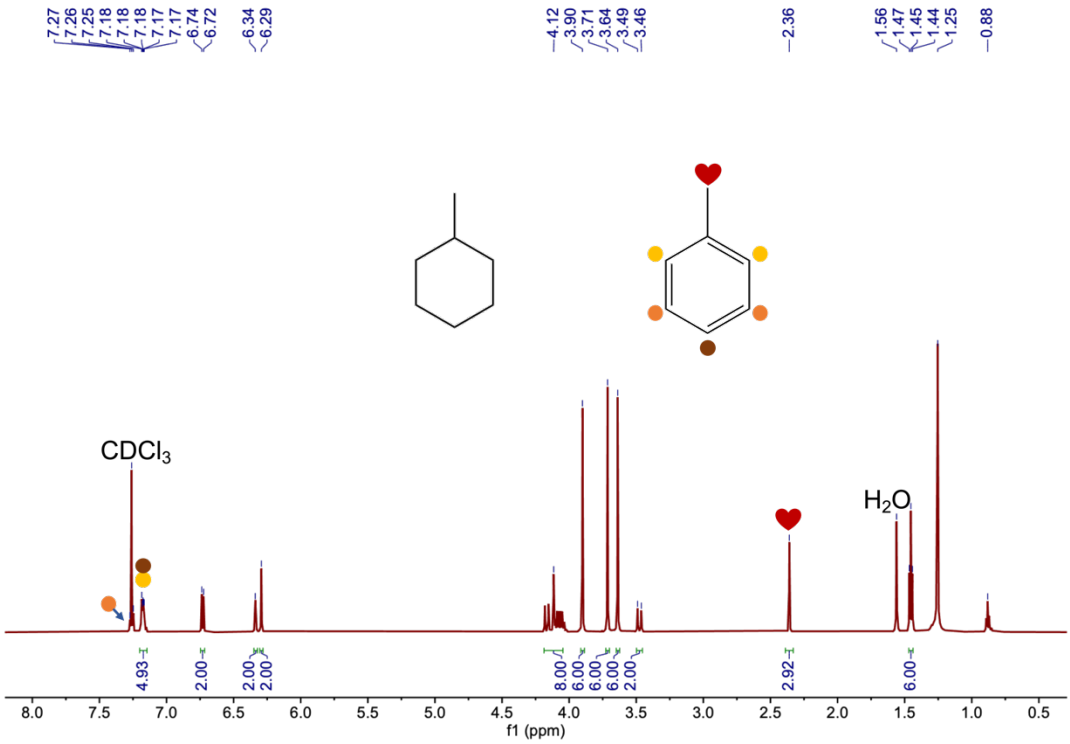

Figure S21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293 K) of **H*α*** after adsorption of the liquid mixture of Tol and MCH (*v*:*v* = 1:1) for 140 min.

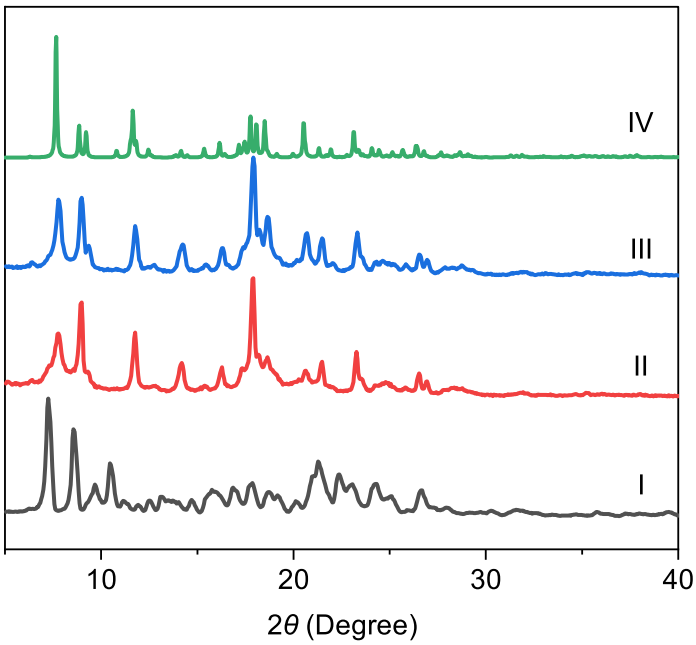

Figure S22. PXRD patterns of: (I) original **H*α***; (II) **H*α*** after adsorption of the Tol liquid; (III) **H*α*** after adsorption of the liquid mixture of Tol and MCH (*v*:*v* = 1:1); (IV) simulated from the single crystal structure of Tol@**H**.

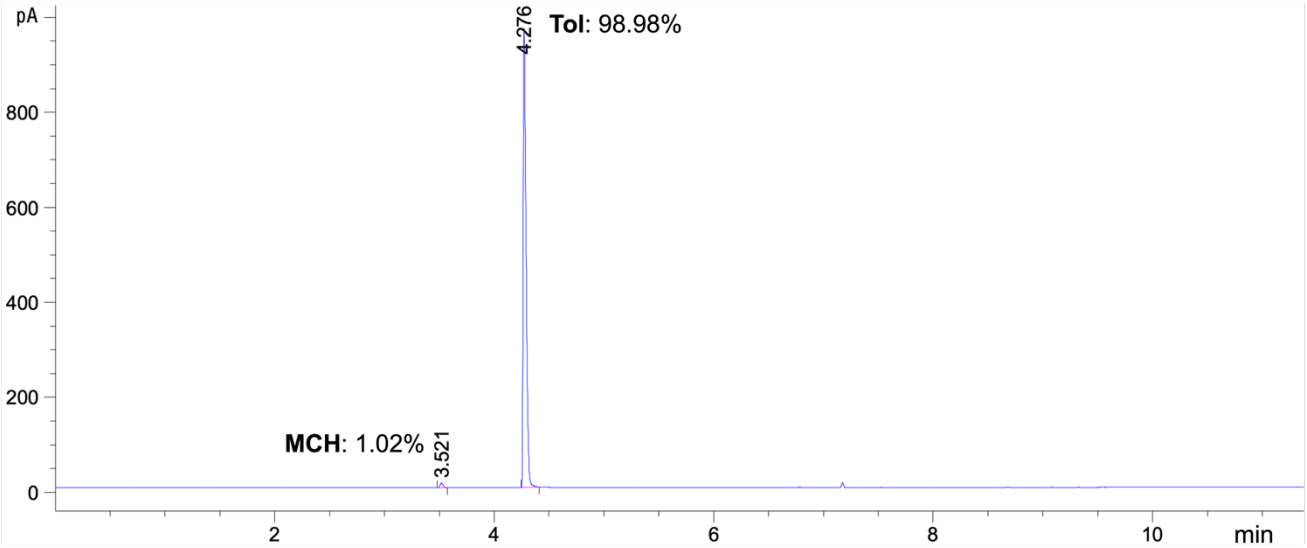

Figure S23. Relative uptakes of Tol and MCH liquids adsorbed by **H*α*** for 140 min using head space gas chromatography.

10. Reference

S1 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.