Separation of Benzene and Cyclohexane by Nonporous Adaptive Crystals of a Hybrid[3]arene

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Supporting Information (18 pages)

1. Materials

All chemicals, including benzene (**Bz**) and cyclohexane (**Cy**), were purchased and used as received. Hybrid[3]arene (**1**) was synthesized as described previously.[S1] Activated crystalline **1** (**1***α*) was recrystallized from acetone and dried under vacuum at 150 °C overnight.

2. Methods

2.1. Solution NMR

Solution ^{1}H NMR spectra were recorded at 400.13 MHz using a Bruker Avance 400 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 K*α* 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

Single crystals of **Bz@1** were grown by slow evaporation: 5 mg of dry **1** were put in a small vial where 1 mL of **Bz** was added. The resultant transparent solution was allowed to evaporate slowly to give 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 K*α* radiation (λ = 0.71073 Å).

2.6. Gas Sorption Measurement

Low-pressure gas adsorption measurements were performed on a Micrometritics Accelerated Surface Area and Porosimetry System (ASAP) 2020 surface area analyzer. Samples were degassed under dynamic vacuum for 12 h at 60 °C prior to each measurement. N_2 isotherms were measured using a liquid nitrogen bath (77 K).

2.7. Vapor Sorption Measurement

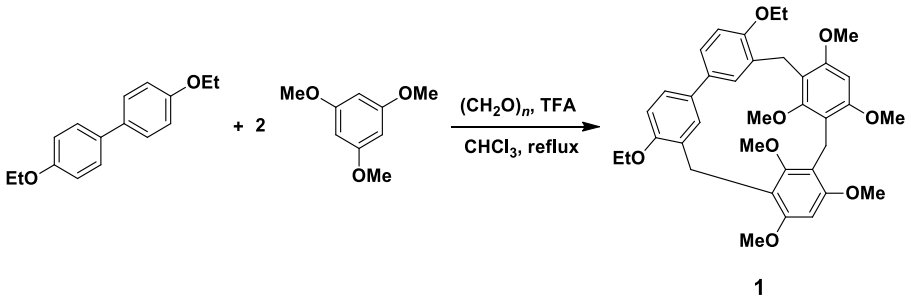
Bz and **Cy** sorption isotherms were measured via a Micromeritic 3Flex instrument. Samples were degassed under dynamic vacuum for 12 hours at 80 °C prior to each measurement. The isotherms were collected at 25 °C by monitoring the volume changes.

2.8. Gas Chromatography

Head Space Gas Chromatographic (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 followed by sampling 1 mL of the headspace. The following GC method was used: the oven was programmed from 50 °C 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).

3. Synthesis of Hybrid[3]arene 1

Scheme S1. Synthetic Route to Hybrid[3]arene **1**



1

Hybrid[3]arene **1** was prepared according to a literature procedure.[S1]

4. Crystallographic Data

Table S1. Experimental single crystal X-ray data for **Bz@1**.

Formula	**Bz@1**
Crystallization Solvent	benzene
Collection Temperature (K)	273
Formula	$C_{43}H_{48}O_8$
Formula Weight	692.81
Crystal System	Triclinic
Space Group	P-1
a [Å]	10.7525(3)
b [Å]	13.2311(4)
c [Å]	15.5424(4)
α [°]	105.2250(10)
β [°]	105.9030(10)
γ [°]	108.3520(10)
V [Å^3]	1865.15(9)
Z	2
D_{calcd} [g cm^{-3}]	1.234
Absorption coefficient (mm^{-1})	0.084
F(000)	740
Theta range [°]	2.90−26.13
Reflections collected / unique	11849 / 7373 [*R*(int) = 0.0158]
Data / restraints / parameters	7373 / 0 / 468
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.1118, wR_2 = 0.1118
R indices (all data)	R_1 = 0.1186, wR_2 = 0.1186
Goodness-of-fit on F^2	1.013
Largest difference peak and hole [e.A^{-3}]	0.414 and -0.341
CCDC	1962323

5. Characterization of Activated 1 Crystals (1*α*)

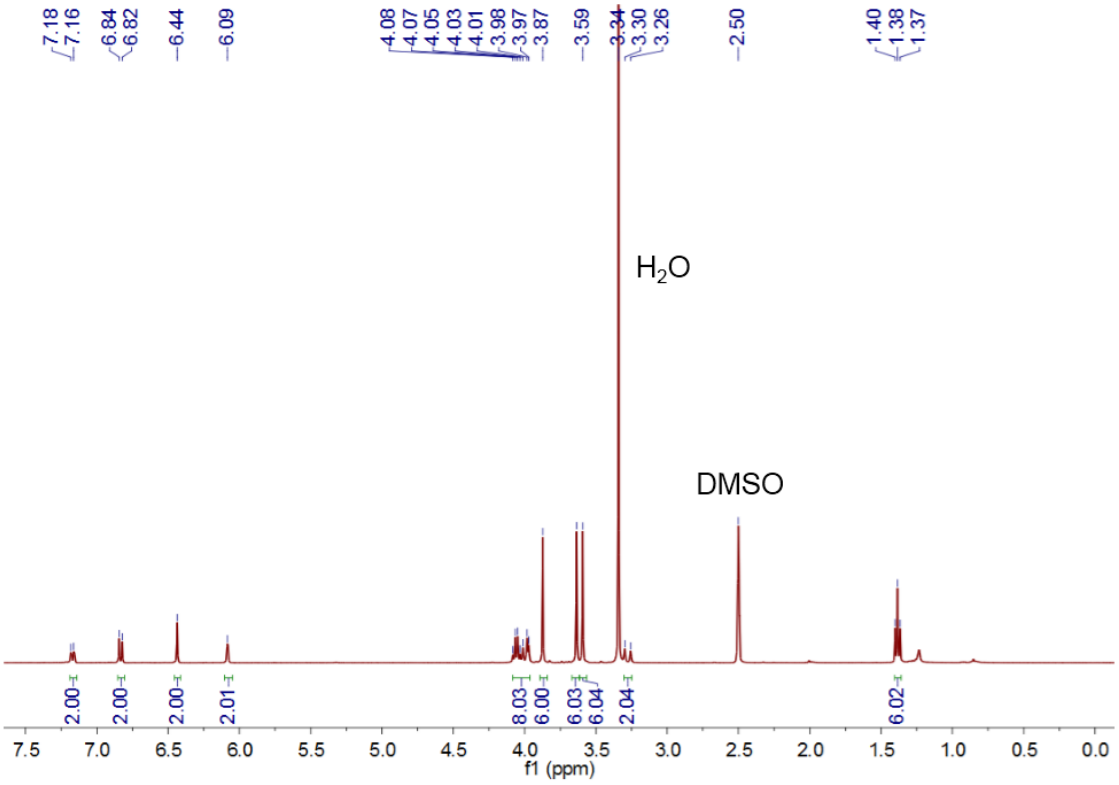


Figure S1. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of **1***α*.

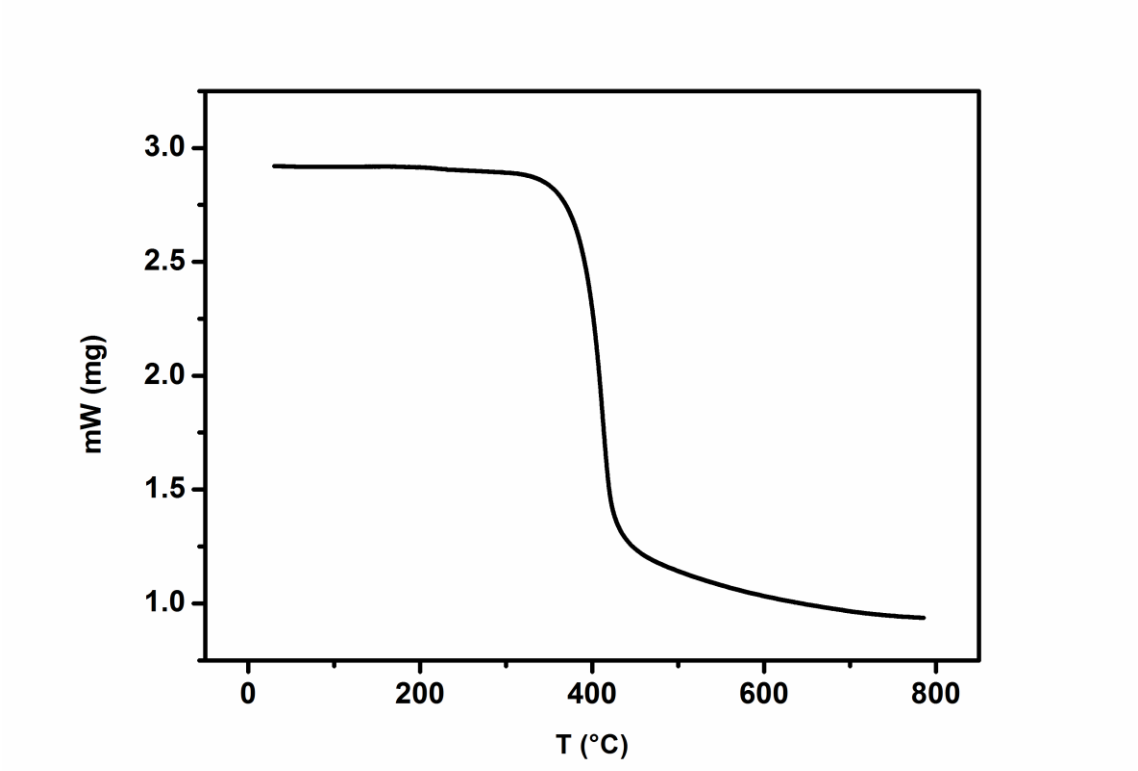


Figure S2. Thermogravimetric analysis of **1***α*.

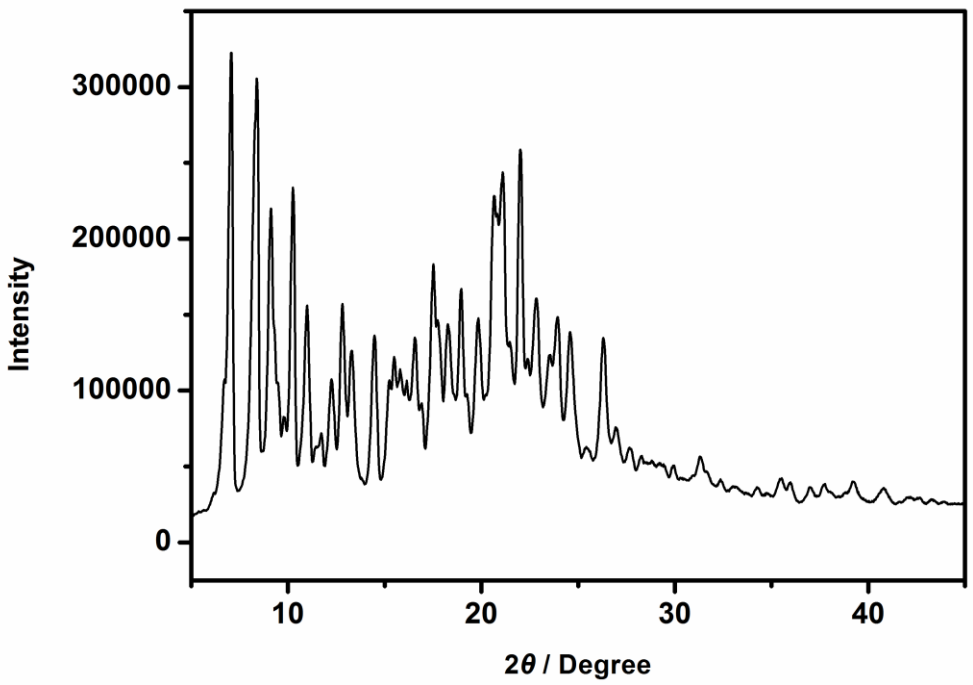


Figure S3. Powder X-ray diffraction pattern of **1***α*.

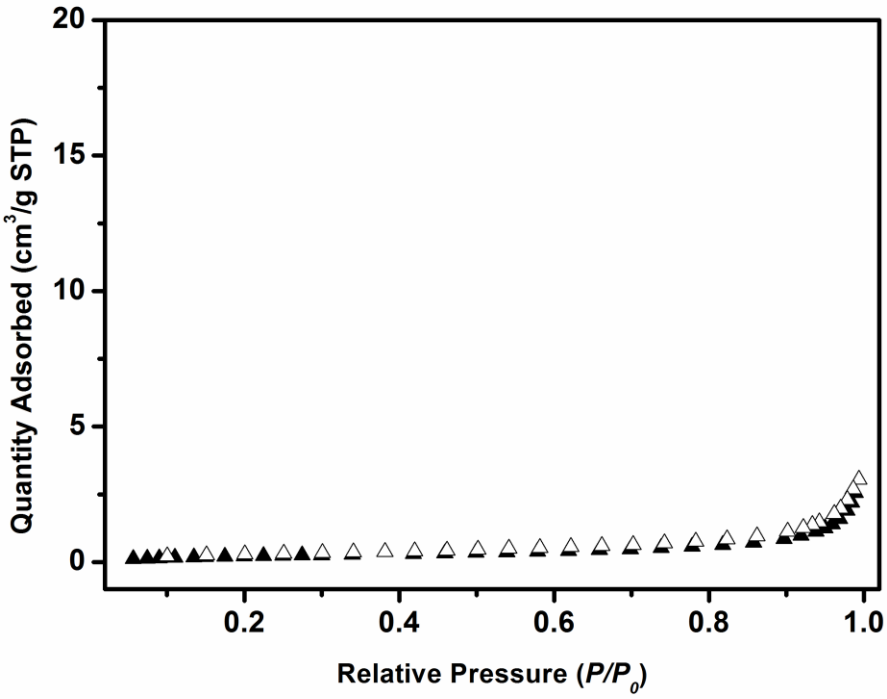


Figure S4. N_2 adsorption isotherm of **1***α*. The BET surface area value is 0.8995 m^2/g. Adsorption, closed symbols; desorption, open symbols.

6. Single-Component Bz/Cy Adsorption Experiments

^{1}H NMR experiments were performed by dissolving **1***α* after vapor sorption in DMSO-d_6. TGA profiles were recorded using **1***α* after vapor sorption.

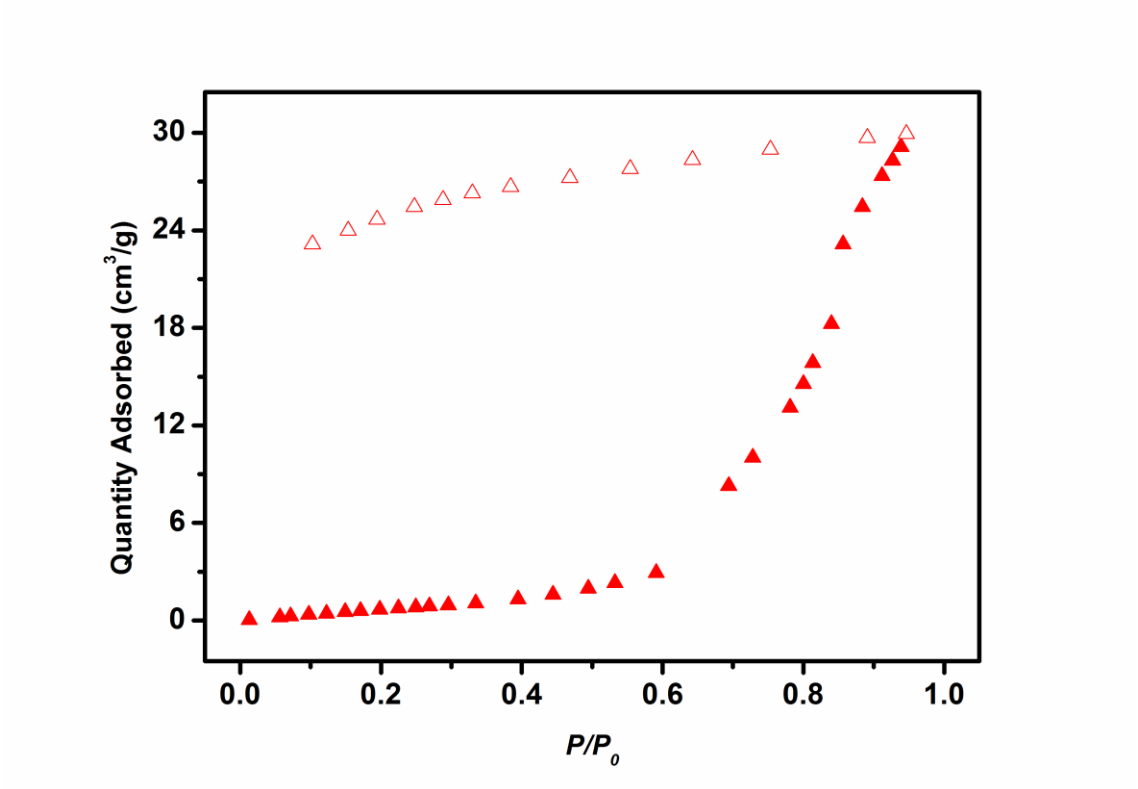


Figure S5. Vapor sorption isotherms of **1***α* towards **Bz**. Adsorption, solid symbols; desorption, open symbols.

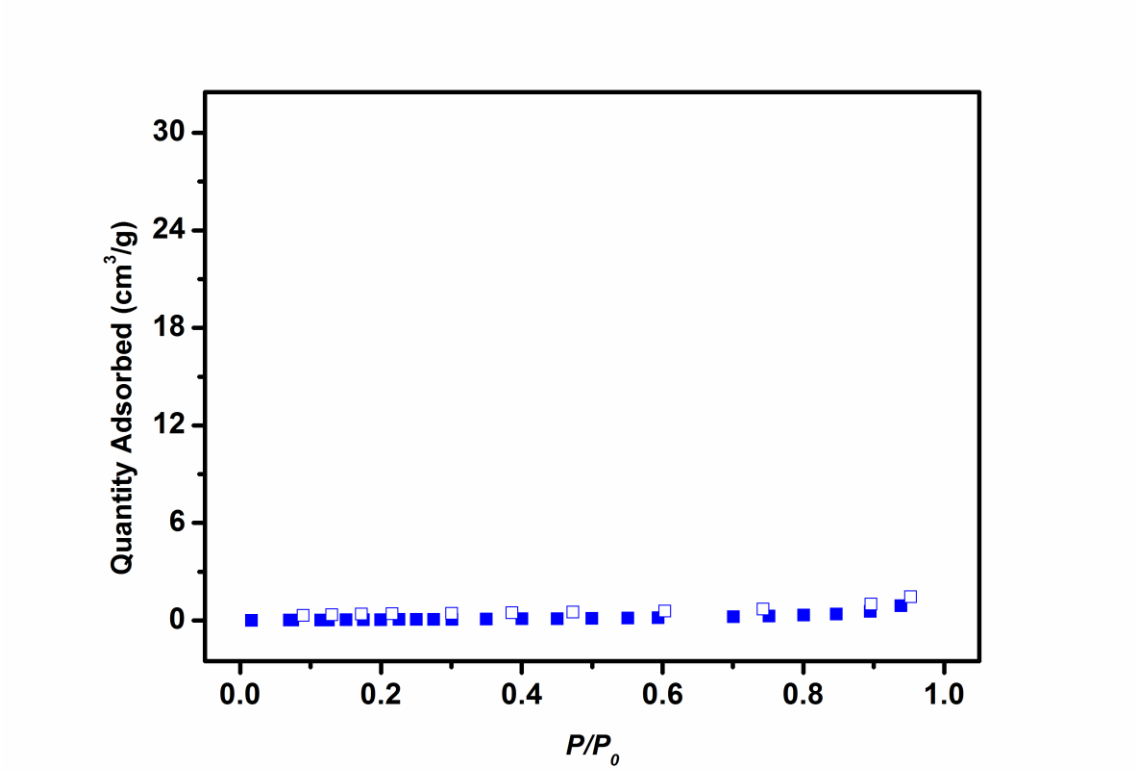


Figure S6. Vapor sorption isotherms of **1***α* towards **Cy**. Adsorption, solid symbols; desorption, open symbols.

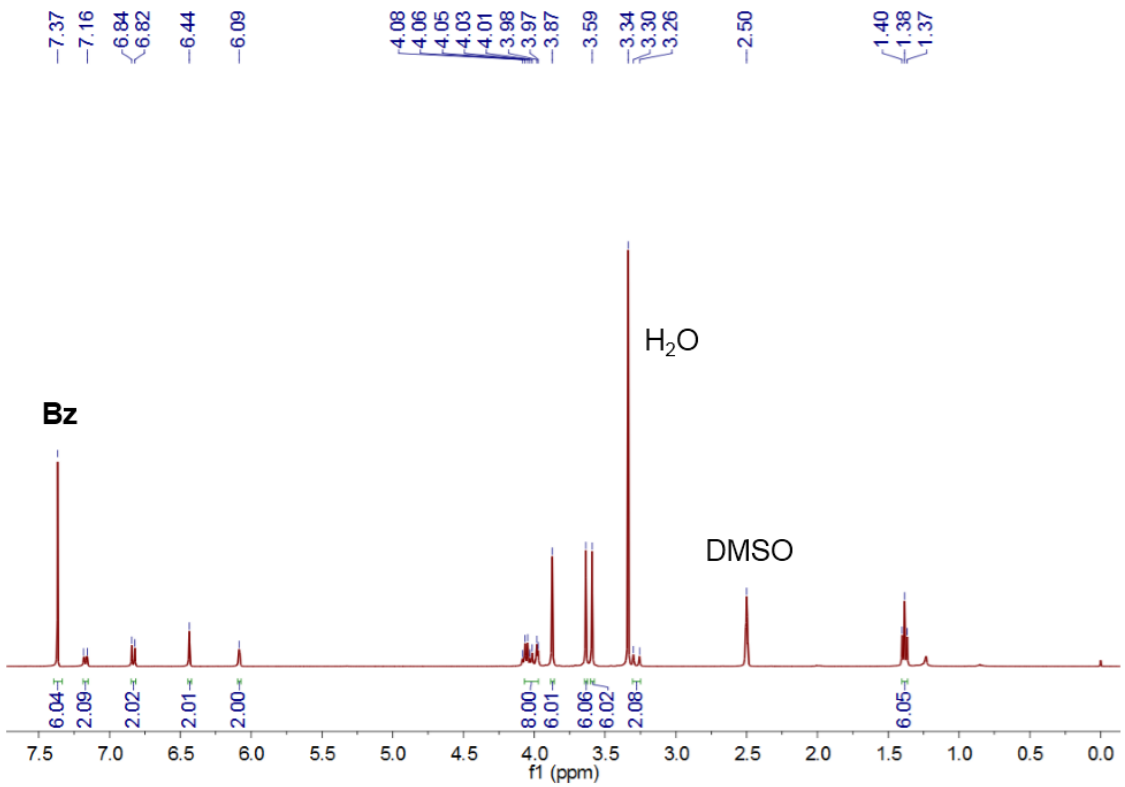


Figure S7. [1]H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of **1**α after sorption of **Bz** vapor for 12 h.

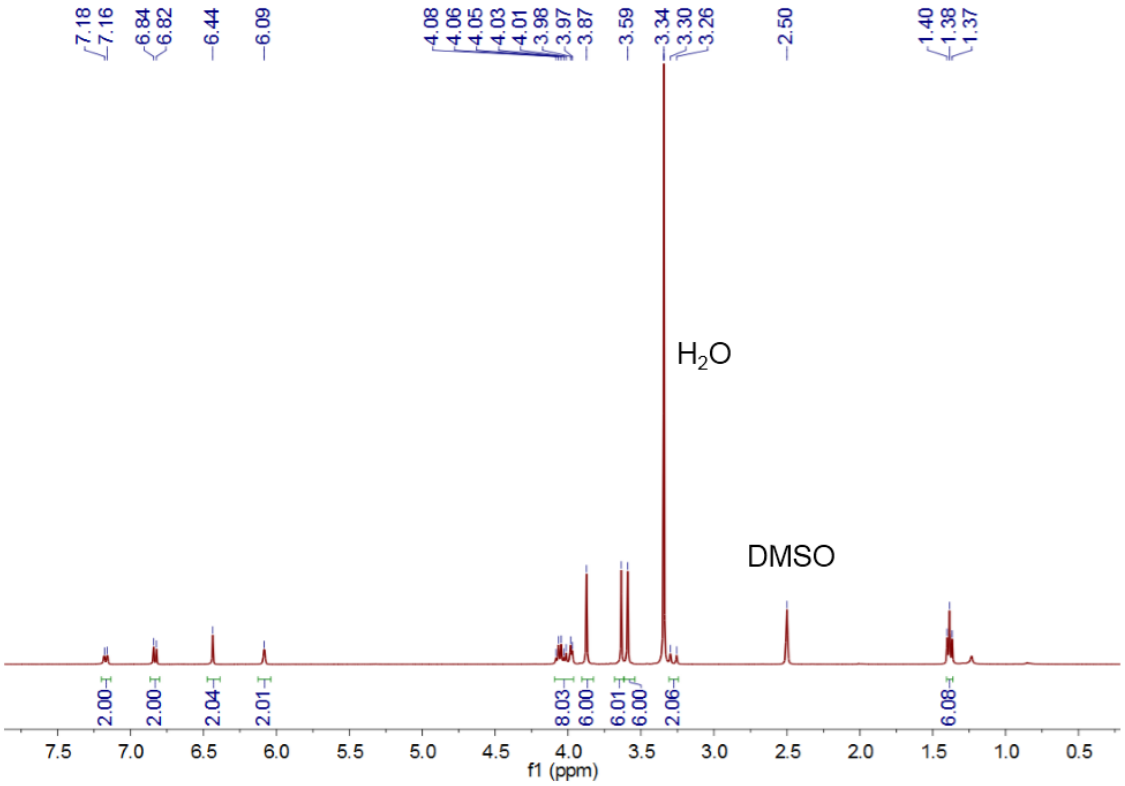


Figure S8. [1]H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of **1**α after sorption of **Cy** vapor for 12 h.

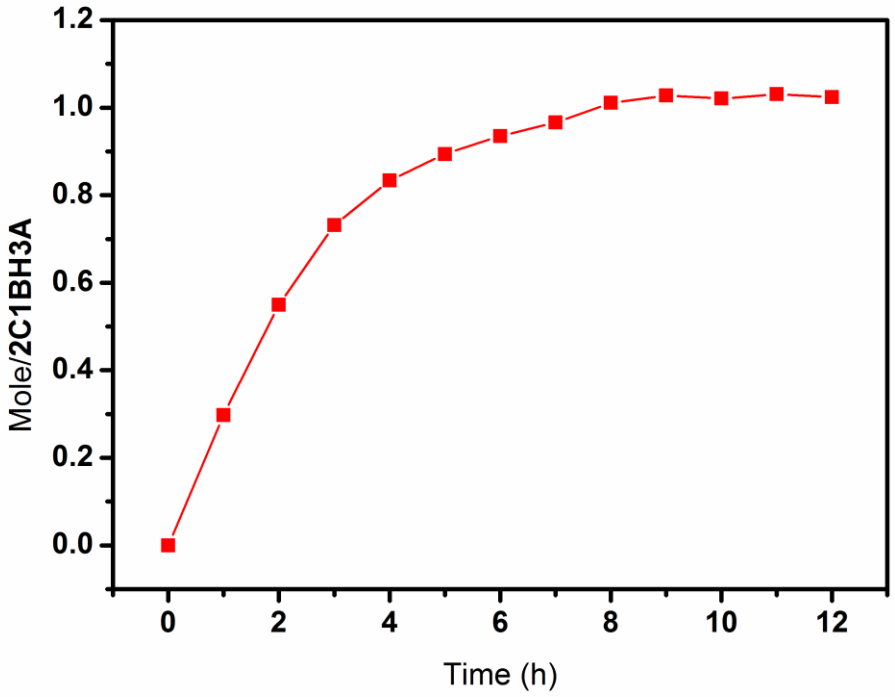


Figure S9. Time-dependent solid−vapor sorption plots of **1***α* for single-component **Bz** vapor.

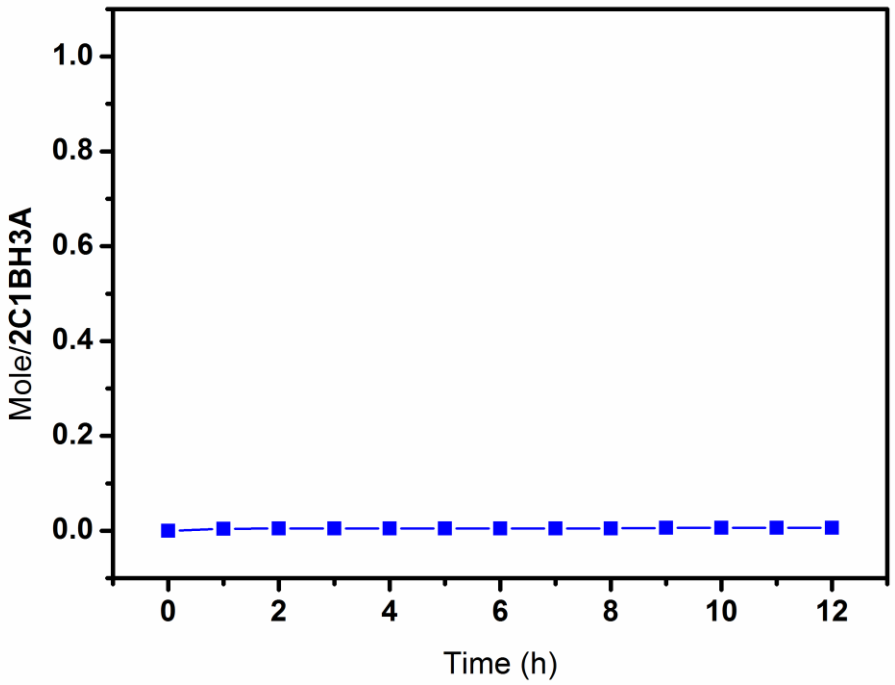


Figure S10. Time-dependent solid−vapor sorption plots of **1***α* for single-component **Cy** vapor.

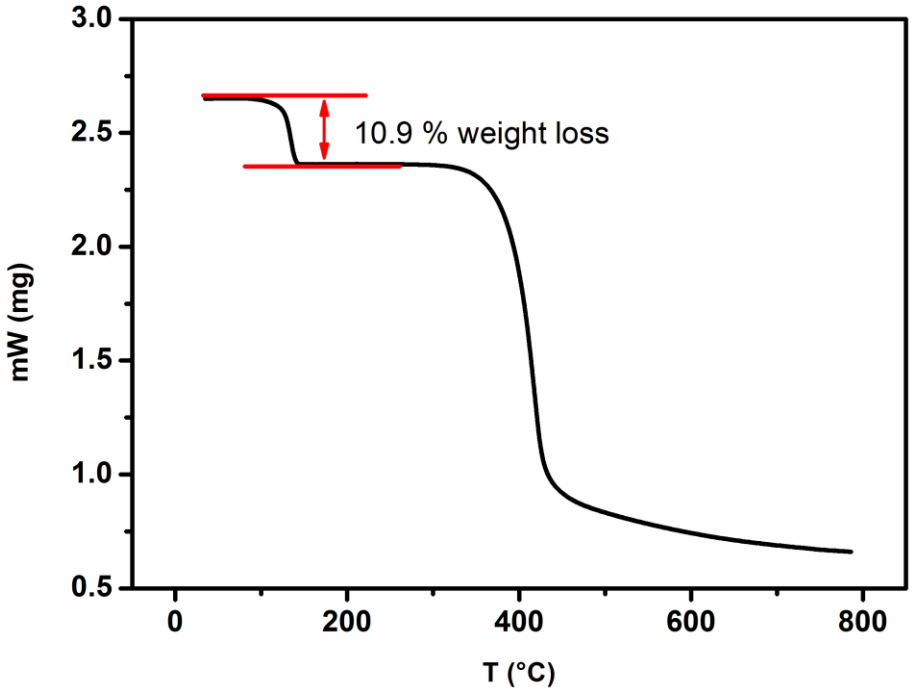


Figure S11. Thermogravimetric analysis of **1***α* after sorption of **Bz** vapor for 12 h. The weight loss below 150 °C can be calculated as one **Bz** molecule per **1** molecule.

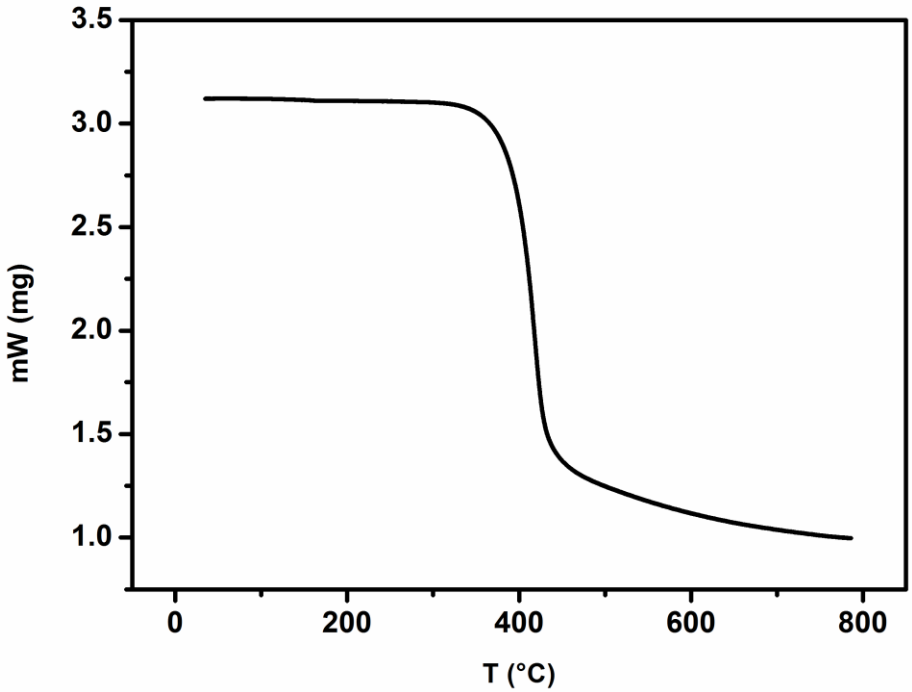


Figure S12. Thermogravimetric analysis of **1***α* after sorption of **Cy** vapor for 12 h.

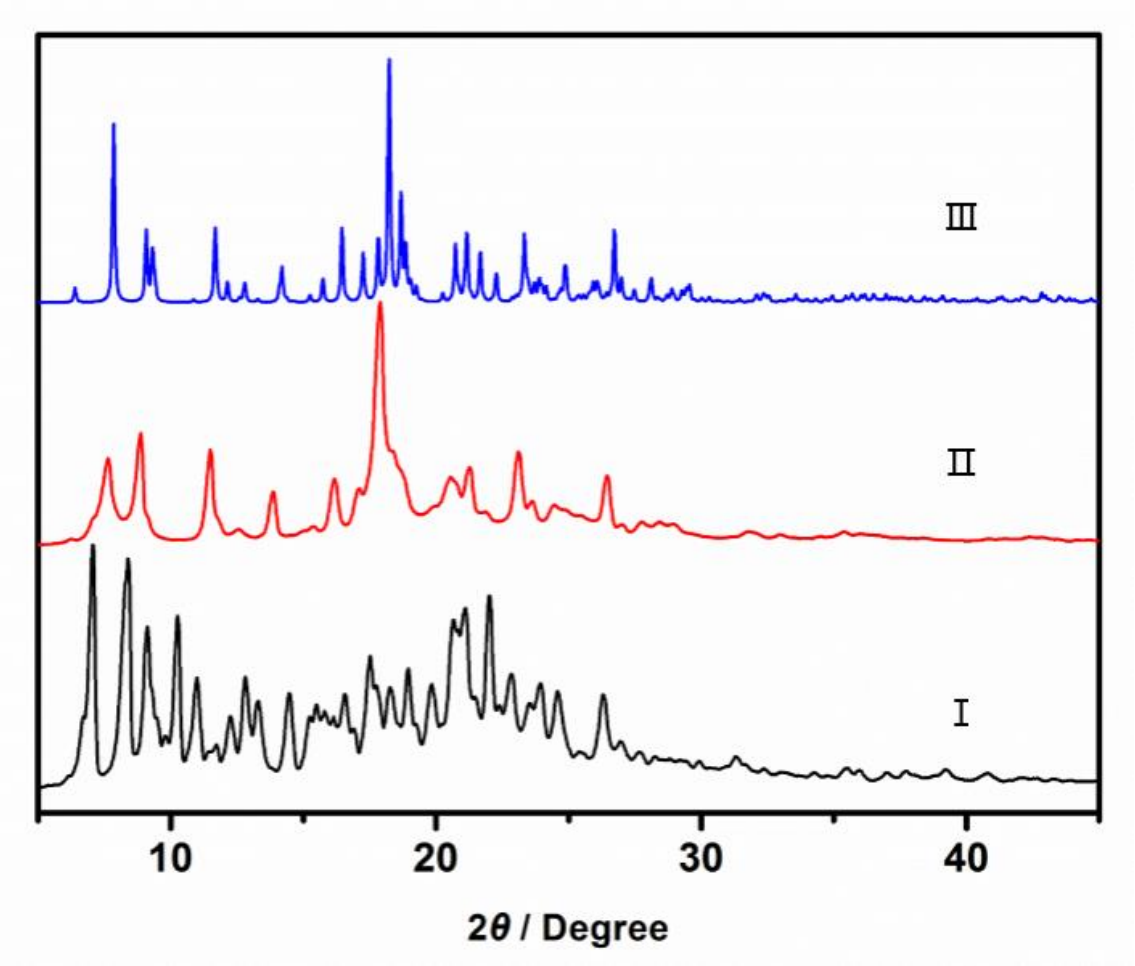


Figure S13. PXRD patterns of **1**: (I) original **1***α*; (II) after adsorption of **Bz** vapor; (III) simulated from single crystal structure of **Bz**@**1**.

7. Noncovalent Interactions Analysis in Single Crystal Structure of Bz@1

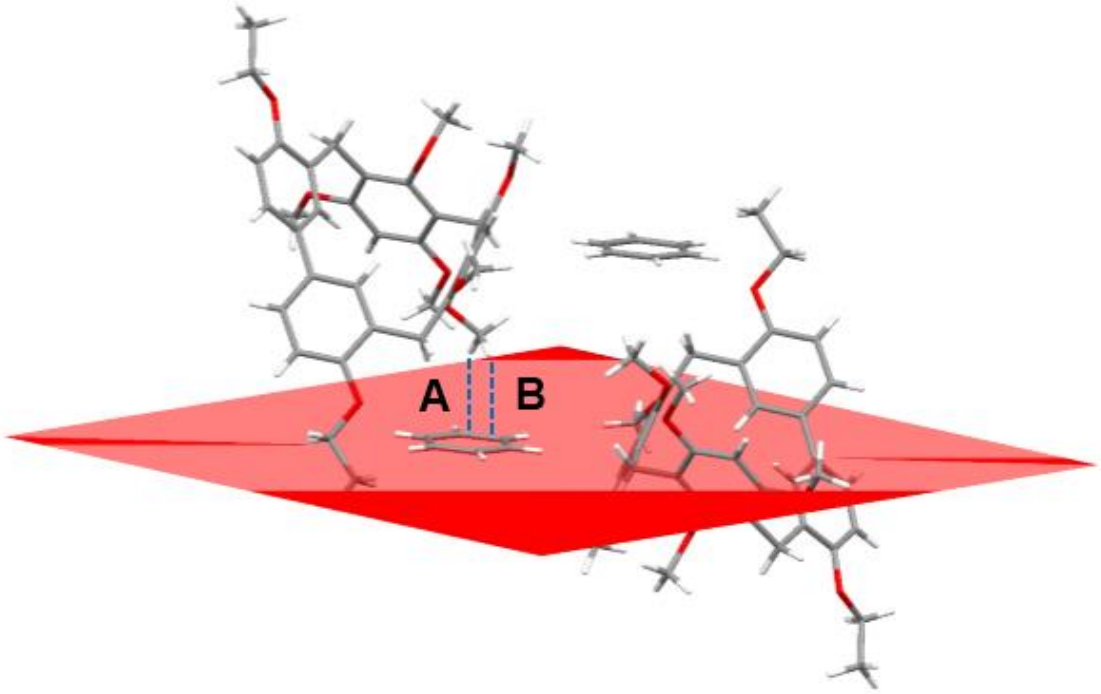


Figure S14. Illustration of C–H···π interactions between two H atoms on the methyl group of **1** and the benzene ring on **Bz**. H–π-plane distances: **A** = 2.712 Å; **B** = 2.932 Å.

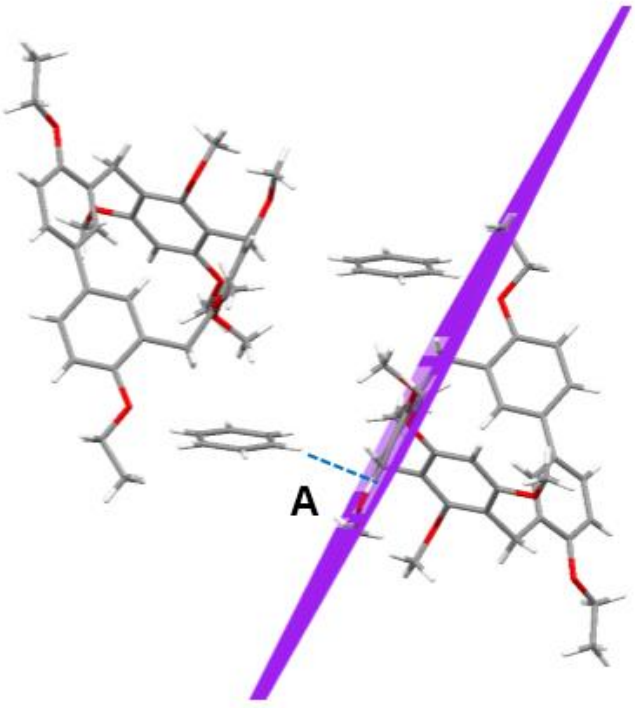


Figure S15. Illustration of a C–H···π interaction between an H atom on **Bz** and a phenyl ring of **1**. H–π-plane distance: **A** = 2.651 Å.

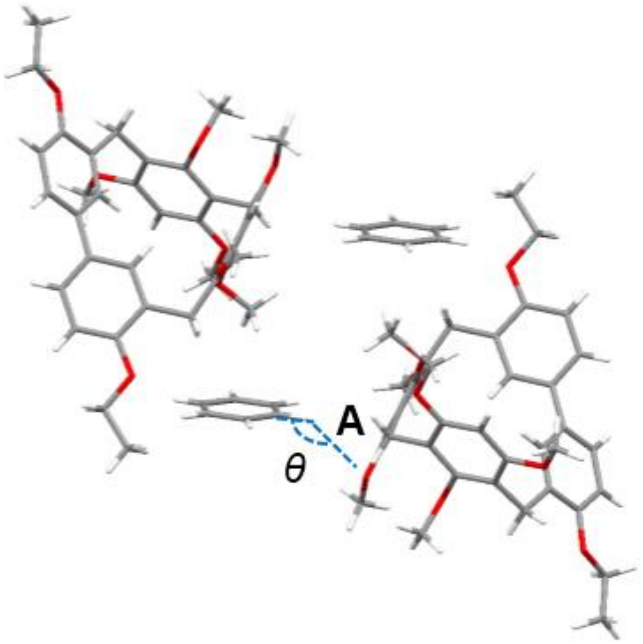


Figure S16. Illustration of a C–H···O interaction between an O atom of **1** and an aromatic H atom of **Bz**. H–O distance: **A** = 2.982 Å; C–H···O angle: θ = 125.34°.

8. Uptake from a Bz/Cy Mixture by 1α

An open 5 mL vial containing 0.0200 g of guest-free **1**α adsorbent was placed in a sealed 20 mL vial containing 1 mL of an equimolar **Bz/Cy** mixture. Uptake by **1**α was measured hour by hour by completely dissolving the crystals and measuring the ratio of **Bz** or **Cy** to **1** by ^{1}H NMR. The relative uptakes of **Bz** and **Cy** by **1**α was also measured by heating the crystals to release the adsorbed vapor and detecting the relative amounts of **Bz** and **Cy** in the released vapor using gas chromatography.

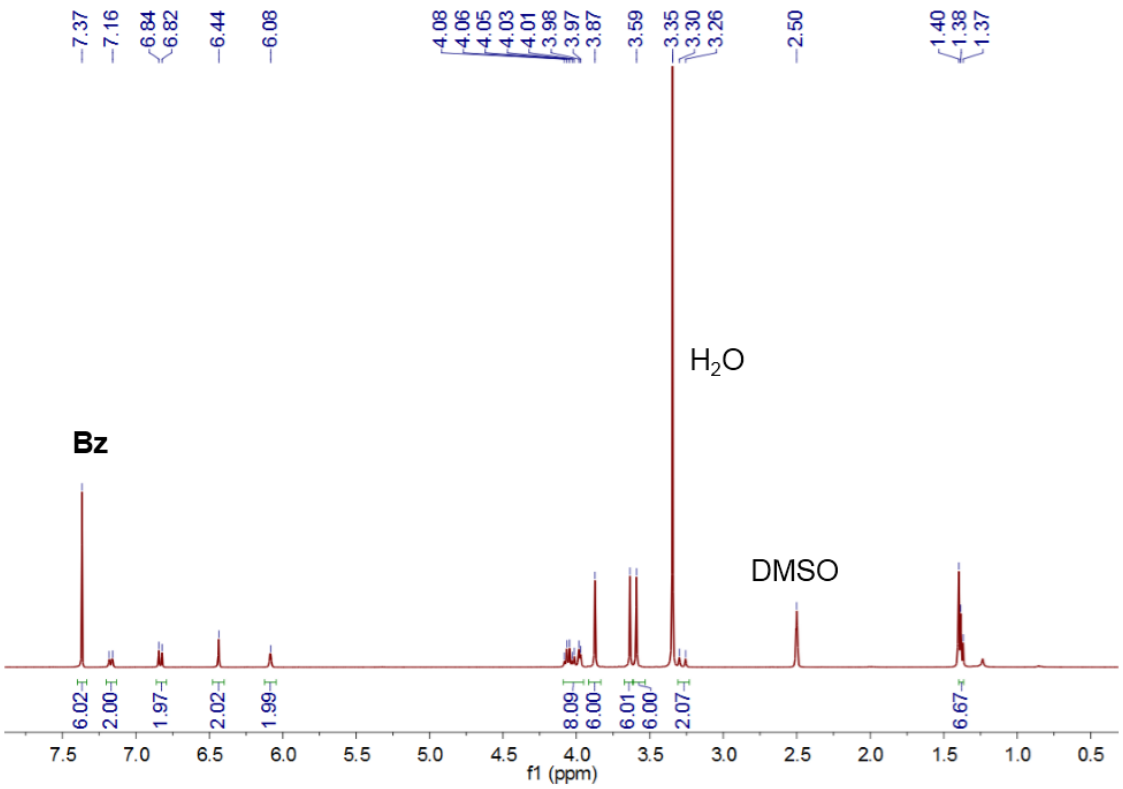


Figure S17. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of **1**α after sorption of an equimolar **Bz**/**Cy** mixture vapor for 12 h.

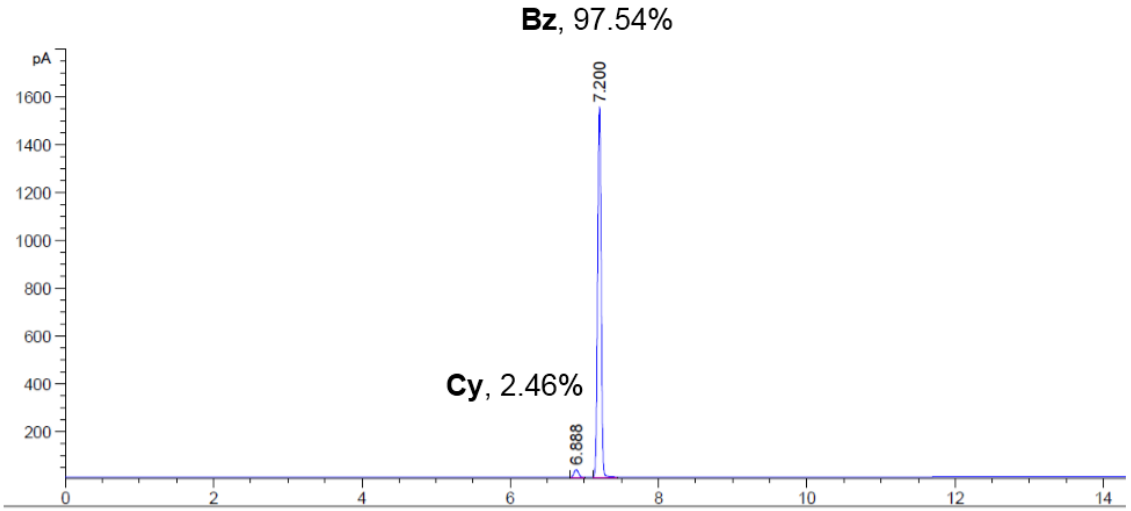


Figure S18. Relative uptakes of **Bz** and **Cy** adsorbed in **1**α for 12 h using head space gas chromatography.

9. Recyclability of 1α

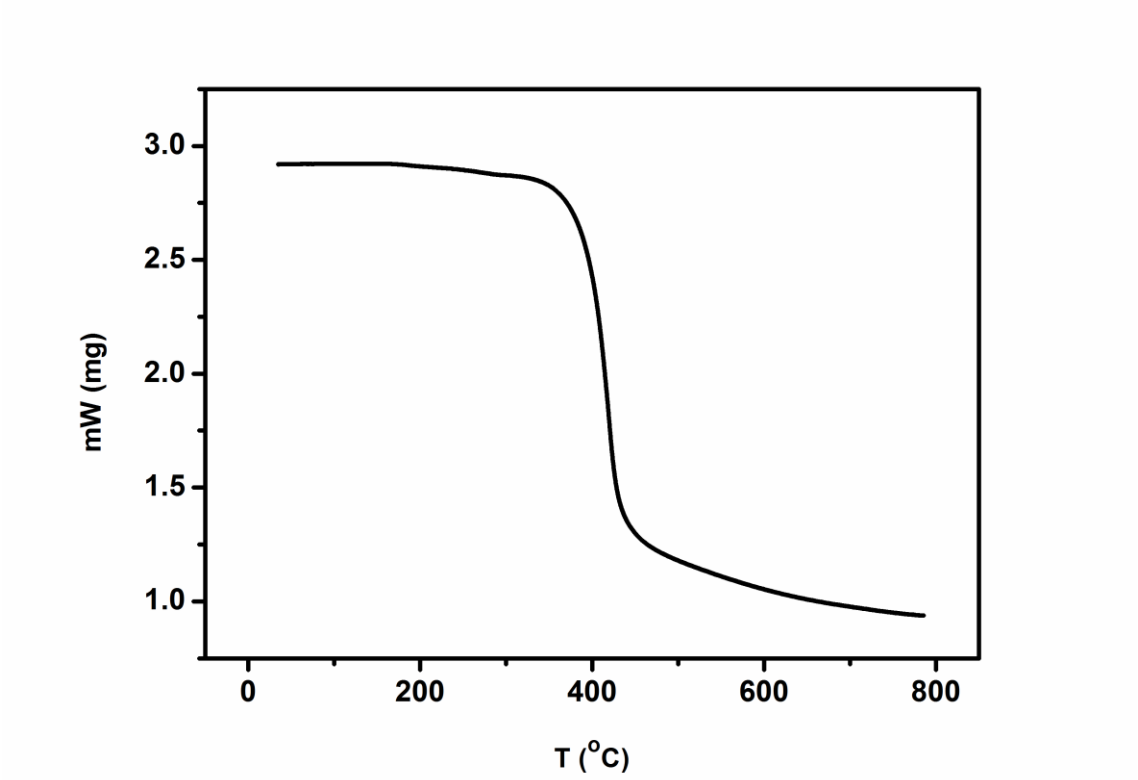


Figure S19. Thermogravimetric analysis of **Bz@1**α after heating at 100 °C under vacuum for 2 h.

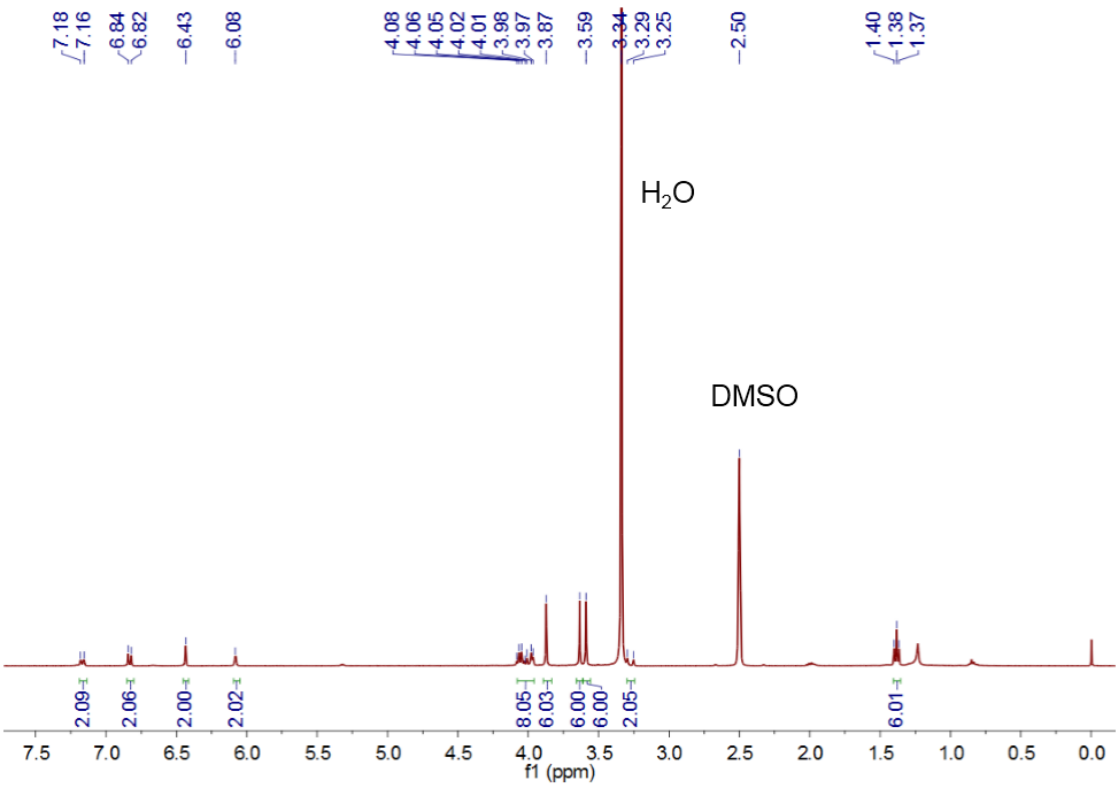


Figure S20. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of **Bz@1**α after heating at 100 °C under vacuum for 2 h.

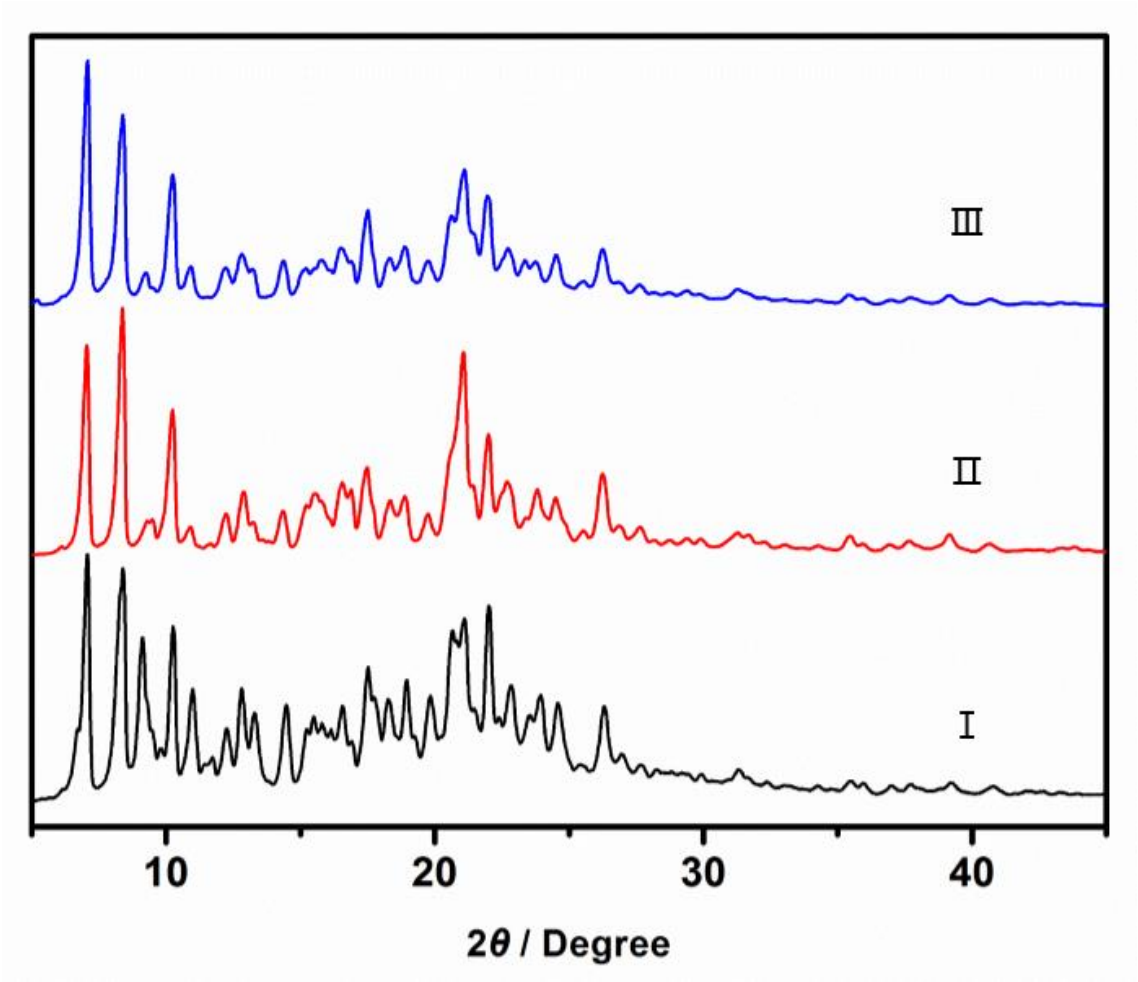


Figure S21. Powder X-ray diffraction patterns of **1**: (I) original **1***α*; (II) **1***α* after heating at 100 °C under vacuum for 2 h; (III) **1***α* after 10 cycles.

10. References

S1. Zhou, J.; Yang, J.; Hua, B.; Shao, L.; Zhang, Z.; Yu, G. The Synthesis, Structure, and Molecular Recognition Properties of a [2]Calix[1]biphenyl-Type Hybrid[3]arene. *Chem. Commun*. **2016**, *52*, 1622–1624.