Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Phenanthrene[2]arene: synthesis and application as nonporous adaptive crystals in separation of Benzene over Cyclohexane

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Contents

1. Materials and Methods.

All reactions were carried out with oven-dried glassware. Commercial reagents were used without further purification. Flash column chromatography was performed on 100-200 mesh silica gel. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DMX400 NMR spectrometer. Melting points were determined using WRR melting point apparatus and were uncorrected. High Resolution atmospheric-pressure chemical ionization mass spectra (APCI-MS) were determined by Bruker Daltonics. Inc, APEX II.

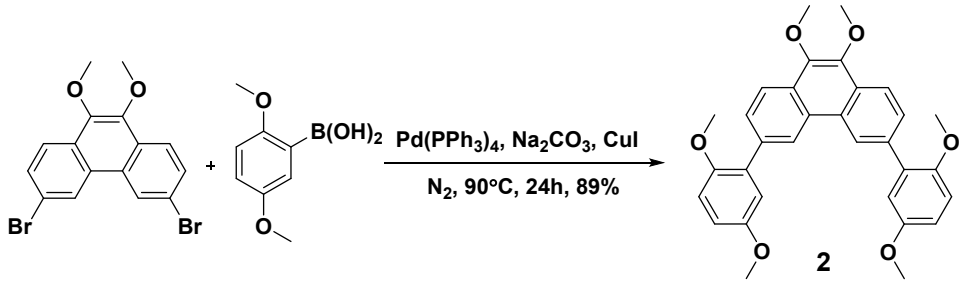
Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultimate-IV X-ray diffractometer operating at 40 kV/30 mA using the Cu Kα line (λ = 1.5418 Å). Data were measured over the range of 5-45° in 5°/min steps over 8 min.

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.

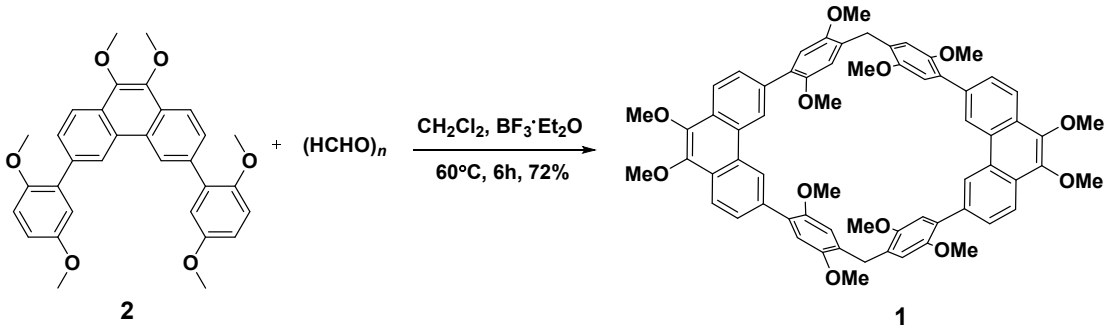
Low-pressure gas adsorption measurements (Gas Sorption Measurement) were performed on a Micrometritics Accelerated Surface Area and Porosimetry System (ASAP) 2020 surface area analyzer. Samples were degassed under dynamic vacuum for 12 h at 60 °C prior to each measurement. N_2 isotherms were measured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

Gas Chromatography Head Space Gas Chromatographic (HS-GC) Analysis: HS-GC measurements were carried out using GC-MS QP-2010 SE instrument configured with an FID detector and a RXT-5 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.

2. Synthesis of New compounds.



Compound 2 A mixture of 3,6-dibromo-9,10-dimethoxyphenanthrene[S1] (3.94 g, 10 mmol), Na_2CO_3 (2.96 g, 28 mmol), 2,5-dimethoxyphenylboronic acid (4.00 g, 22 mmol), and catalytic amount of CuI (21 mg) and tetrakis(triphenylphosphine)-palladium (320 mg) in 100 mL dioxane and water (v/v = 5:1) in a flask was stirred at 90 °C for 24 h under N_2. After evaporating the solvents, resulting mixture was extracted with dichloromethane (3 × 50 mL) and then washed with water and brine successively. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The residue was purified by column chromatography on silica gel with dichloromethane/ Petroleum ether as eluent (4:1) to afford compound **2** (4.54 g, yield 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 2H), 8.26 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 2.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.90 (dd, *J* = 8.9, 3.0 Hz, 2H), 4.12 (s, 6H), 3.84 (s, 6H), 3.78 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 151.0, 144.1, 136.0, 132.0, 128.7, 128.6, 128.2, 123.5, 121.7, 117.1, 113.2, 112.9, 61.1, 56.5, 55.9. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{32}H_{31}O_6$, 511.2121; found, 511.2128.



Phenanthrene[2]arene 1 To a mixture of **2** (1.02 g, 2.0 mmol) and paraformaldehyde (180 mg, 6.0 mmol) in dichloromethane (150 mL) was added catalytic amount of boron trifluoride diethyl etherate (0.3 mL, 2.4 mmol). The mixture was stirred at 60 °C for 6

h. Then the reaction was quenched by the addition of 150 mL water. The organic layer was separated and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was separated by column chromatography on silica gel (eluent: 3:1 DCM/Petroleum ether) to give **1** (752 mg, 72%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 4H), 8.27 (d, J = 8.4 Hz, 4H), 7.78 (d, J = 8.5 Hz, 4H), 6.97 (s, 8H), 4.12 (s, 12H), 4.09 (s, 4H), 3.89 (s, 12H), 3.69 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 150.6, 144.0, 136.1, 129.7, 129.5, 128.5, 128.1, 124.1, 121.9, 115.4, 113.9, 61.1, 56.7, 56.2, 22.6. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{66}H_{61}O_{12}$, 1045.4163; found, 1045.4165.

3. ^{1}H NMR and ^{13}C NMR Spectral of New compounds.

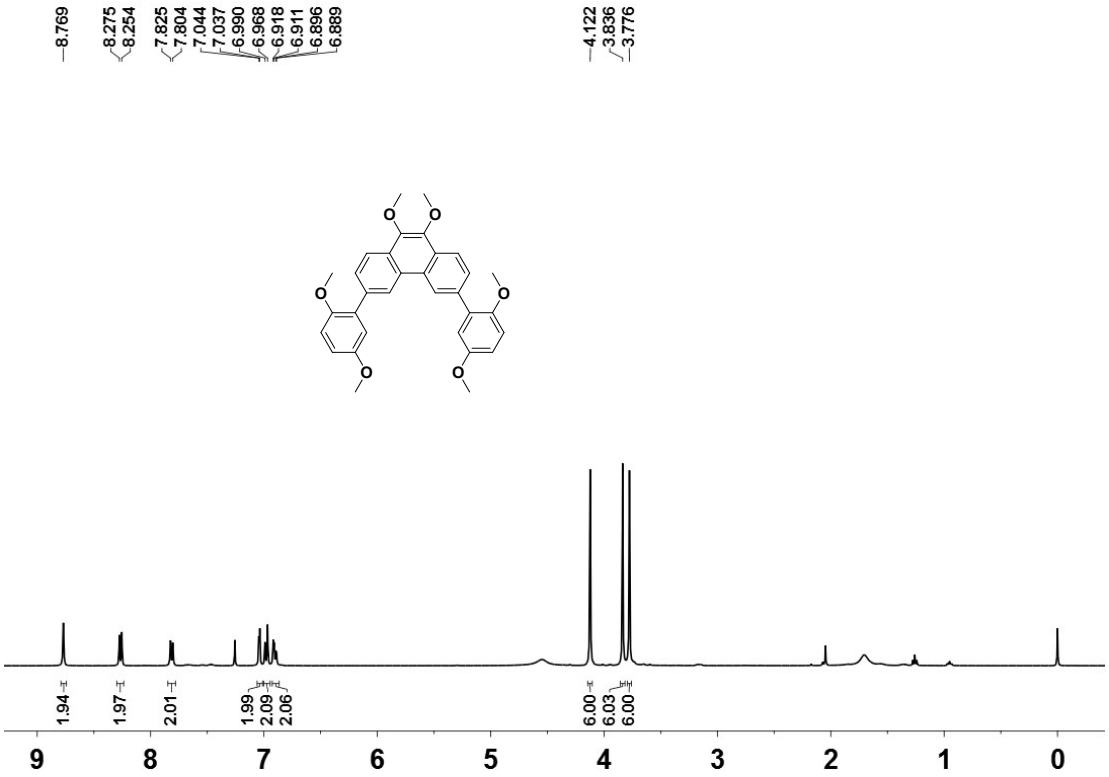


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2**.

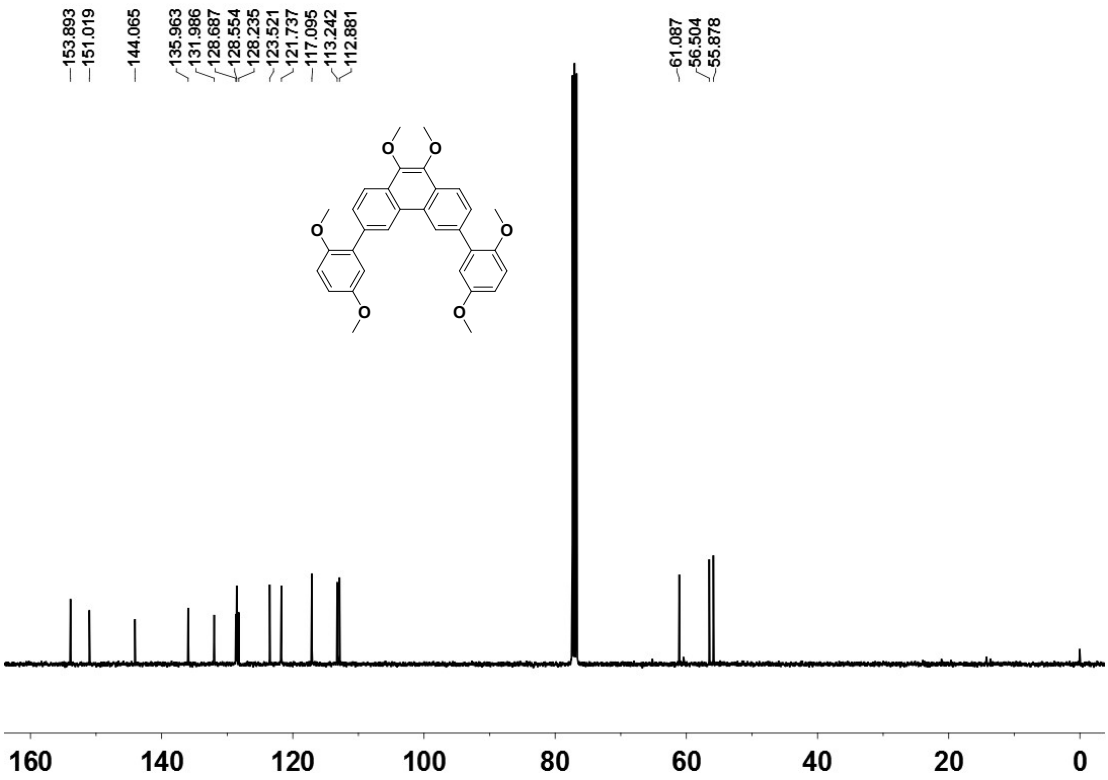


Figure S2. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298K) of **2**.

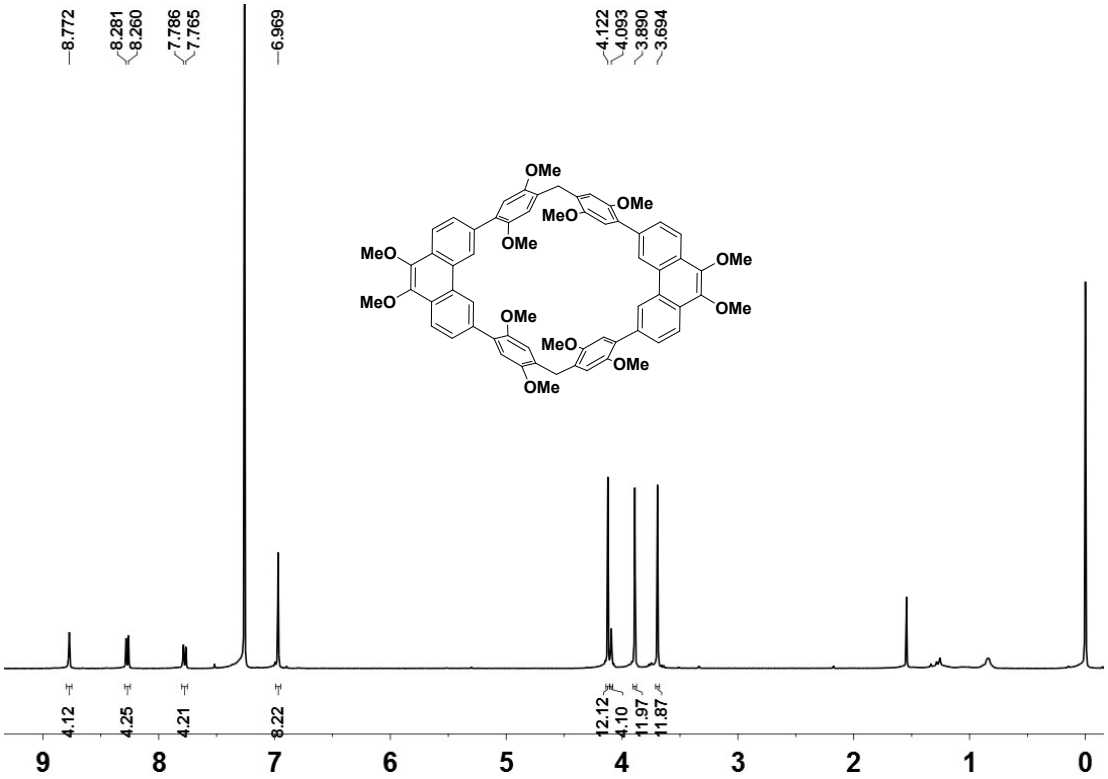


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of host **1**.

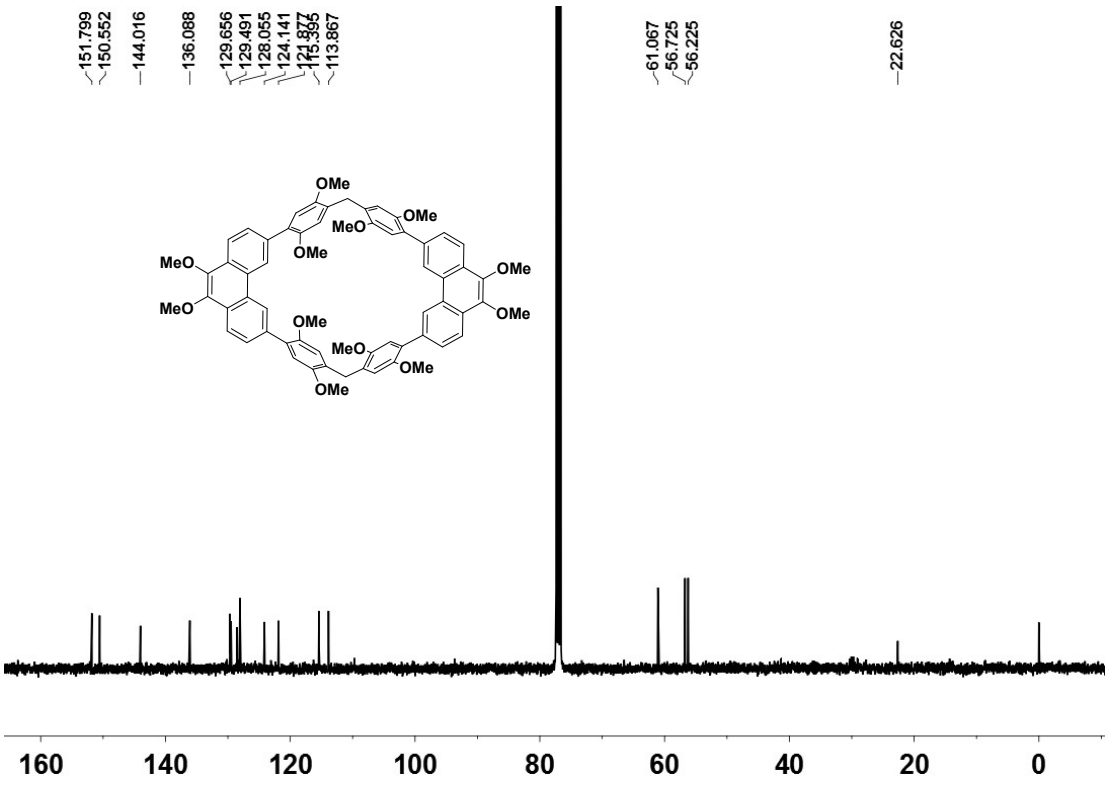


Figure S4.^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298K) of host **1**.

4. Characterization of Activated 1 Crystals

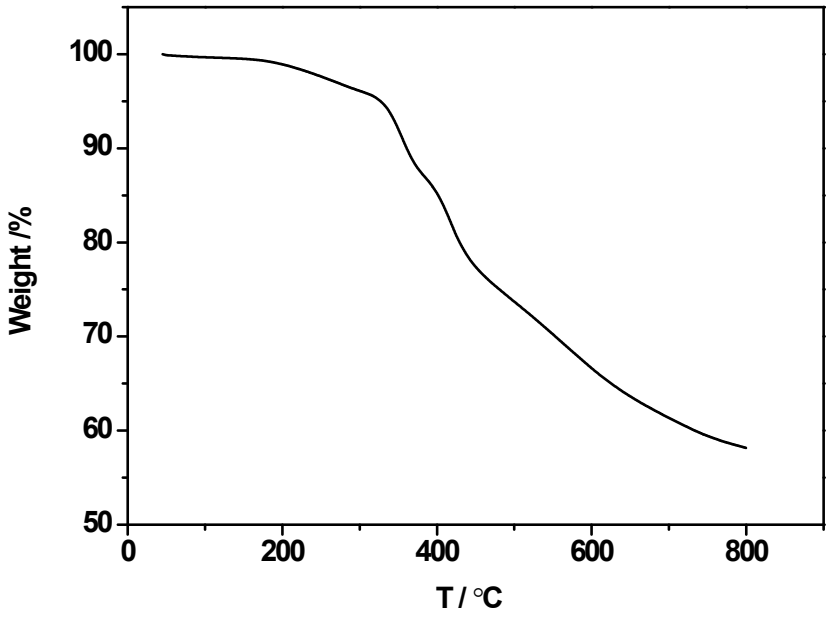


Figure S5. Thermogravimetric analysis of **1**.

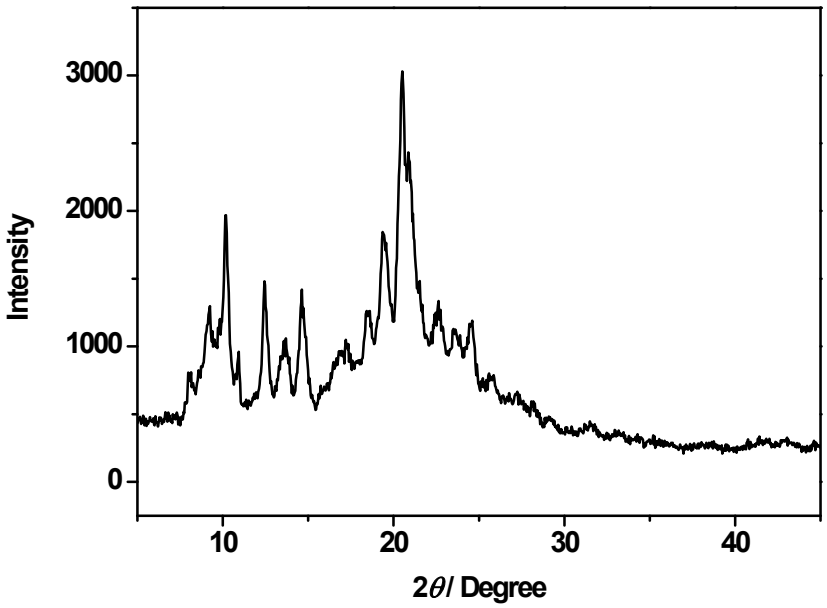


Figure S6. Powder X-ray diffraction pattern of **1**.

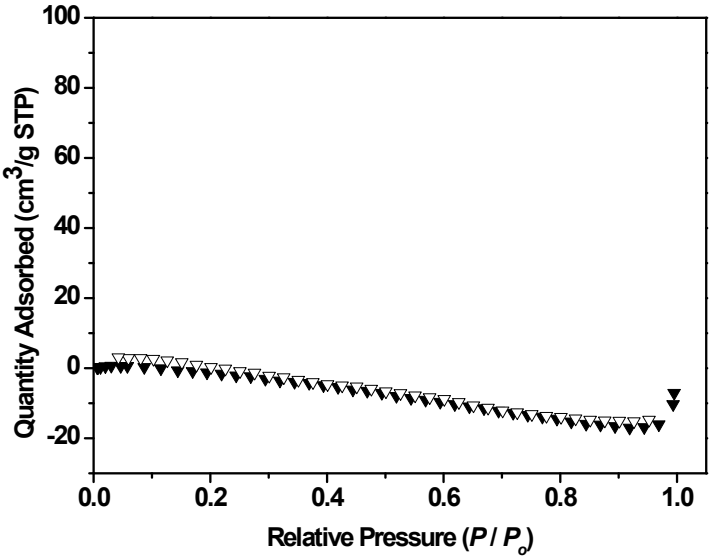


Figure S7. N_2 adsorption isotherm of **1**. The BET surface area value is 4.9971 m^2/g. Adsorption, closed symbols; desorption, open symbols.

5. Single-Component PhH/Cy Adsorption Experiments

In a typical solid-vapor picoline isomers adsorption experiment, an open vial (3 mL) containing 5 mg of activated guest-free **1** crystals was placed into a sealed vial (20 mL) containing 1 mL of **PhH** or **Cy** (single-component adsorption). The adsorption process was monitored over time by measured weight and then completely dissolving a portion of the crystals in $CDCl_3$ and measuring ^1H NMR spectra. TGA profiles were recorded using **1** after vapor sorption.

The calculation between the increased weight and the predicted amount of guest from single-component adsorption.

Mole ratio : host **1** = (Increased weight / molecule weight of **PhH** or **Cy**) : (5 mg / molecule weight of host **1**)

The calculation between the measured weight loss and the predicted amount of guest loss from TGA analysis.

Mole ratio : host **1** = (weight loss% / molecule weight of **PhH** or **Cy**) :[(100%-weight loss%)] / molecule weight of host **1**)

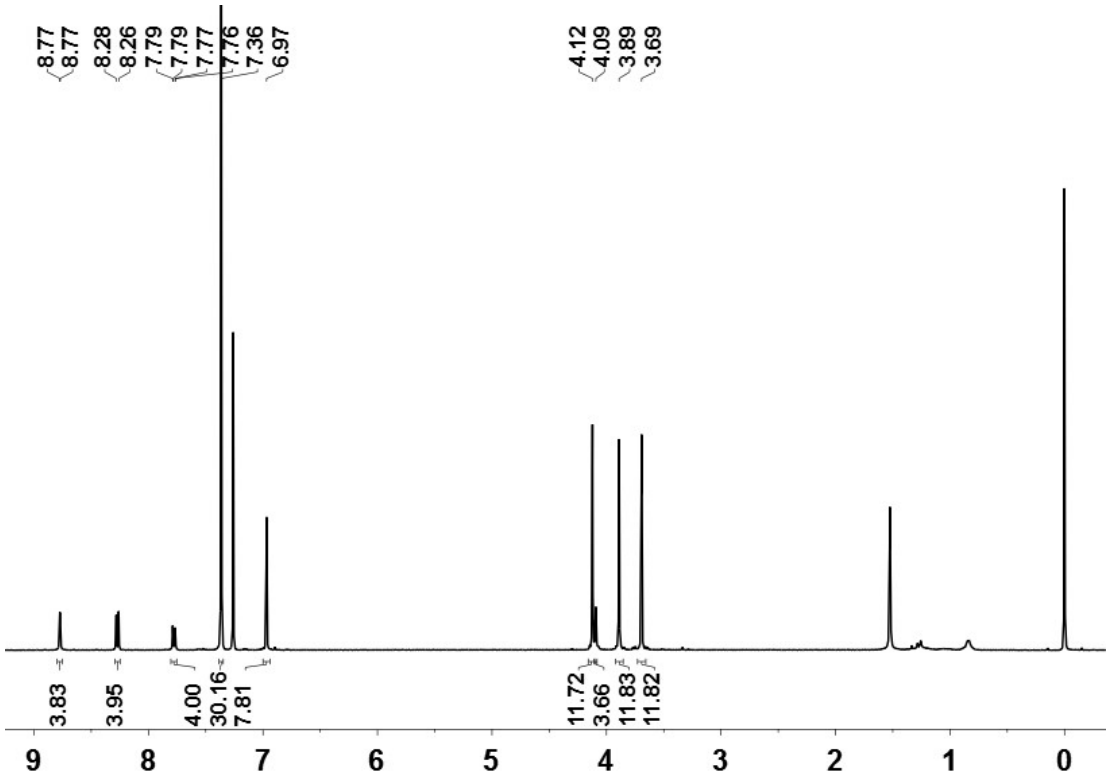


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of activated **1** after sorption of **PhH** vapor for 6 h.

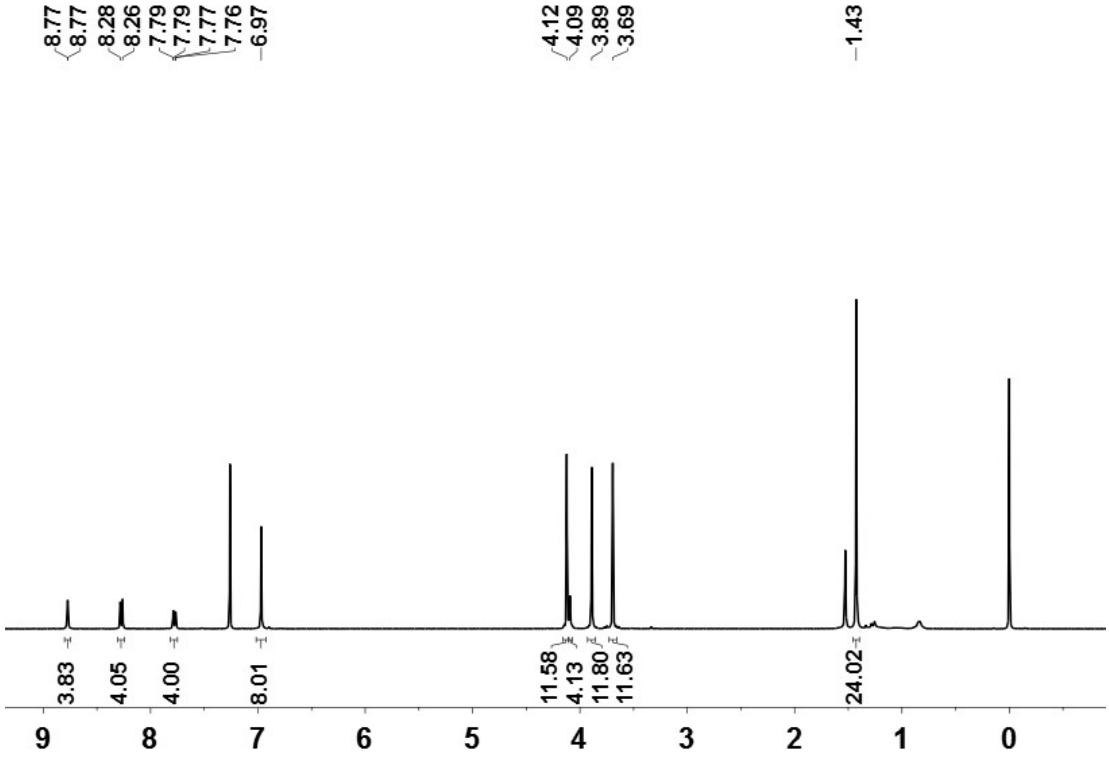


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of activated **1** after sorption of **Cy** vapor for 6 h.

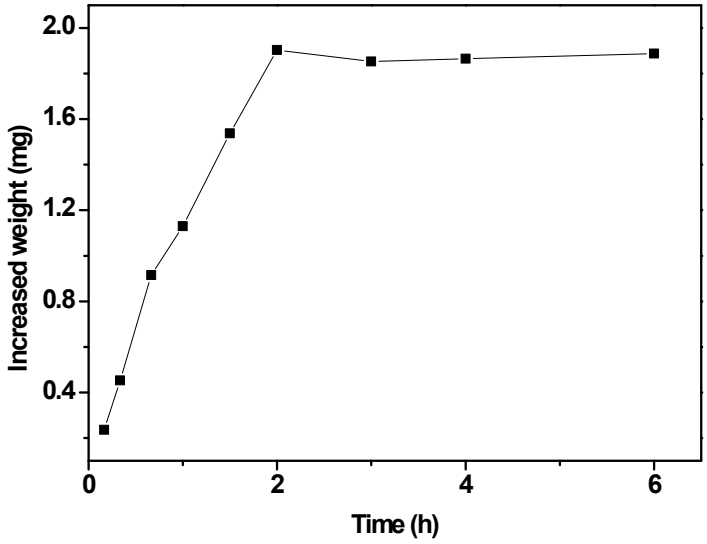


Figure S10. Time-dependent solid-vapor sorption plots of **1** for single-component **PhH** vapor.

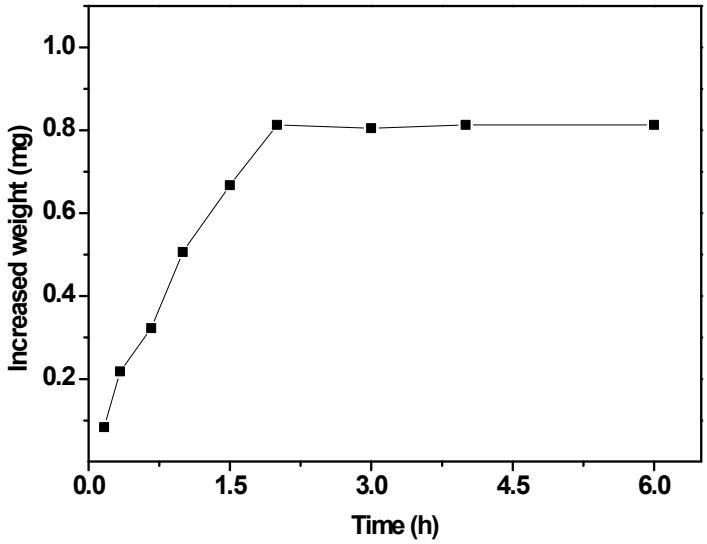
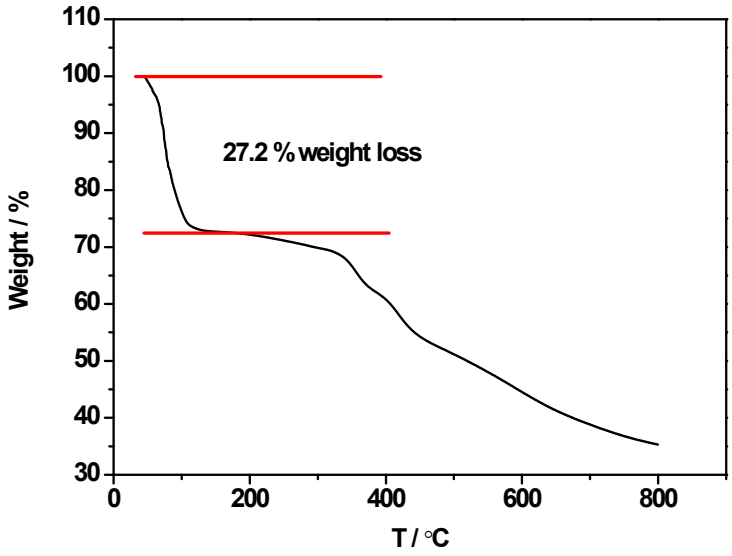
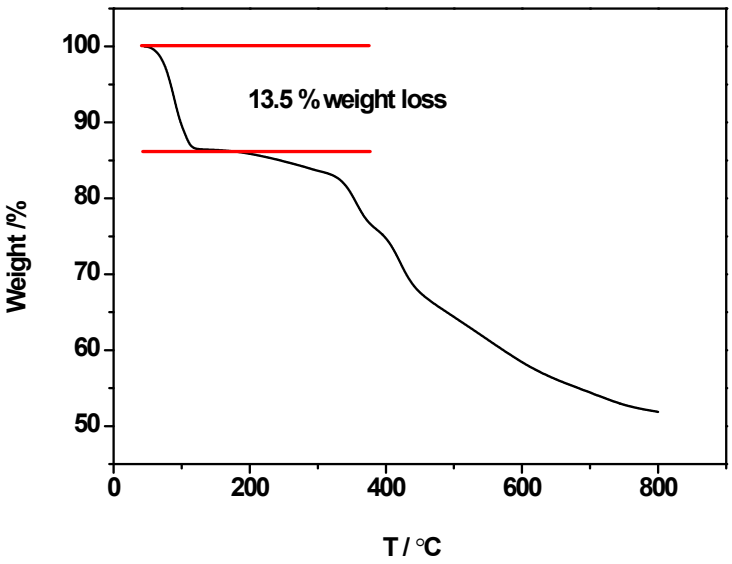


Figure S11. Time-dependent solid-vapor sorption plots of **1** for single-component **Cy** vapor.



1	27.3%
2	27.2%
3	27.2%
average	27.2%
error	0.047

Figure S12. Thermogravimetric analysis of **1** after sorption of **PhH** vapor for 6 h. The weight loss from 55 to 123 °C corresponded to the release of five **PhH** molecules per **1**.



1	13.5%
2	13.5%
3	13.7%
average	13.56%
error	0.095

Figure S13. Thermogravimetric analysis of **1** after sorption of **Cy** vapor for 6 h. The weight loss from 58 to 127 °C corresponded to the release of two **Cy** molecules per **1**.

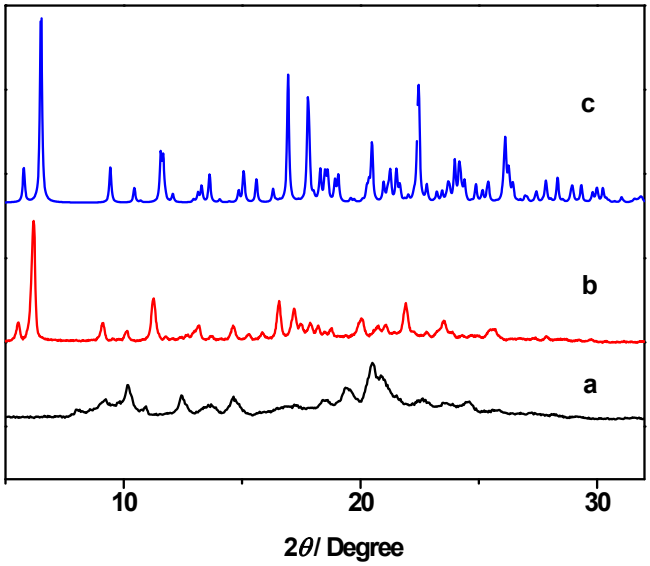


Figure S14. PXRD patterns of **1**: (a) original activated **1**; (b) after adsorption of **PhH** vapor; (c) simulated from single crystal structure of **1@PhH$_4$**.

6. Uptake from a PhH/Cy Mixture by activated 1

An open 5 mL vial containing 10mg of guest-free **1** adsorbent was placed in a sealed 20 mL vial containing 1 mL of an equimolar **PhH/Cy** mixture. Uptake by **1** was measured hour by hour by completely dissolving the crystals and measuring the ratio of **PhH** or **Cy** to **1** by ^{1}H NMR. The relative uptakes of **PhH** and **Cy** by **1** was also measured by heating the crystals to release the adsorbed vapor and detecting the relative amounts of **PhH** and **Cy** in the released vapor using gas chromatography.

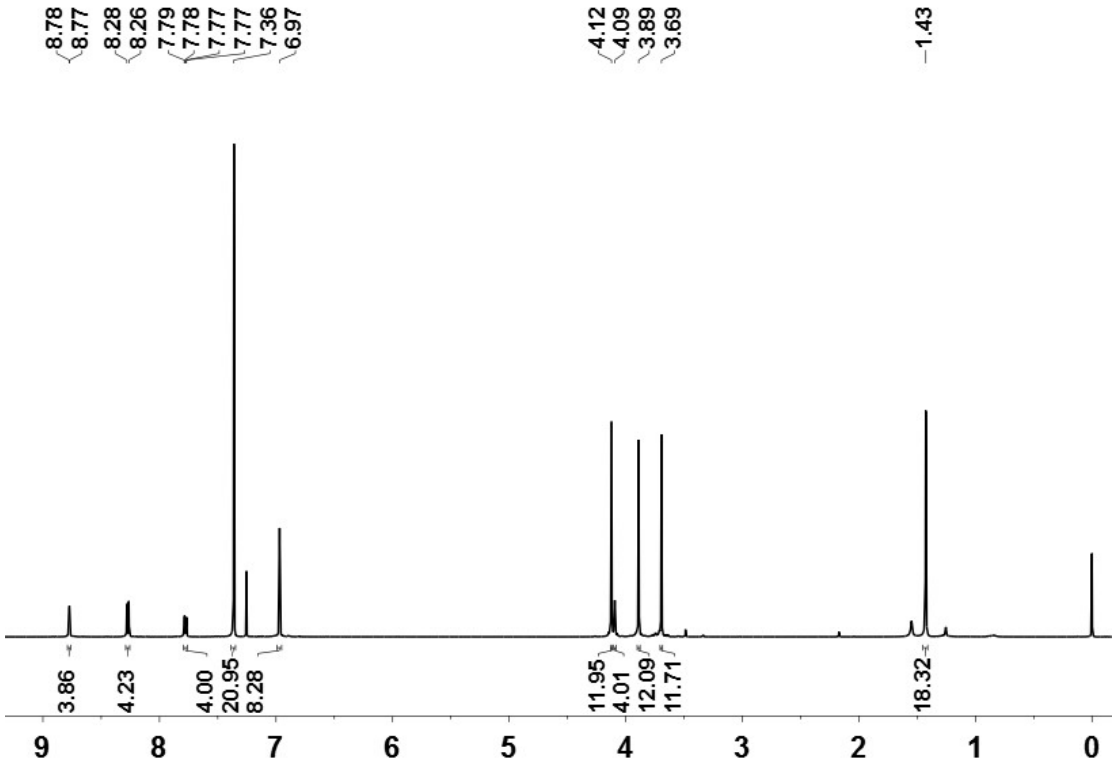


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **1** after sorption of an equimolar **PhH/Cy** mixture vapor for 10 h.

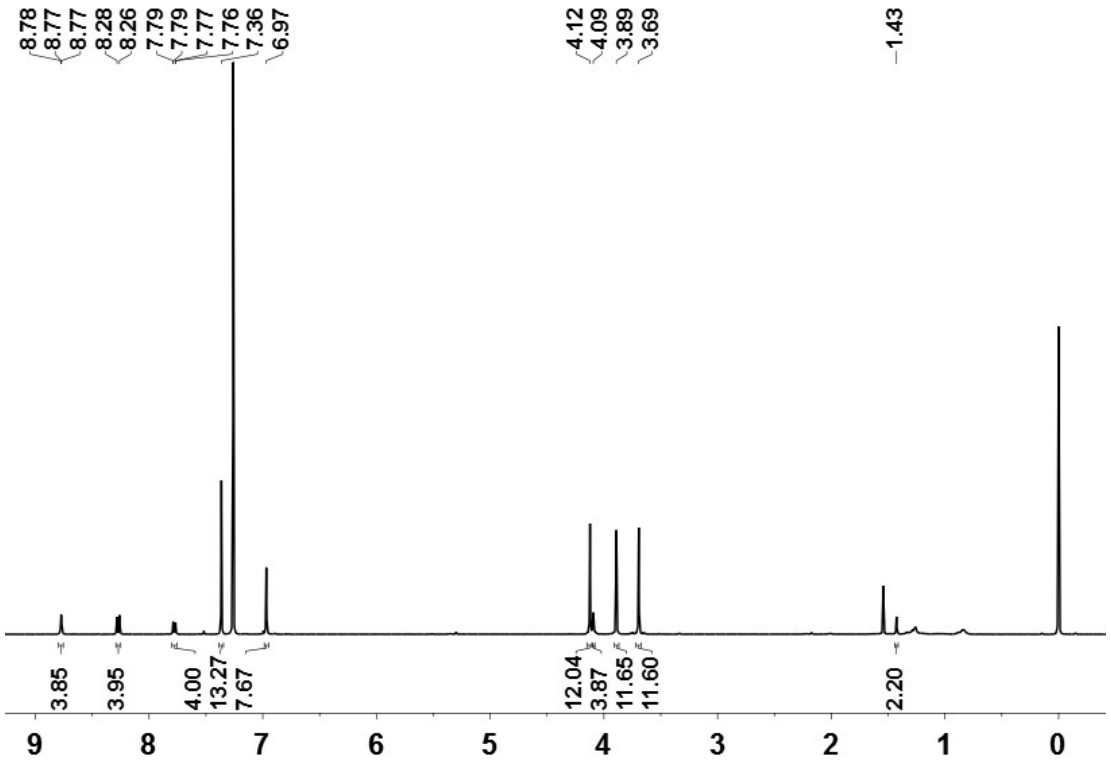


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **1** after sorption of an equimolar **PhH/Cy** mixture vapor for 10 h and then placed at room temperature for **4** hours.

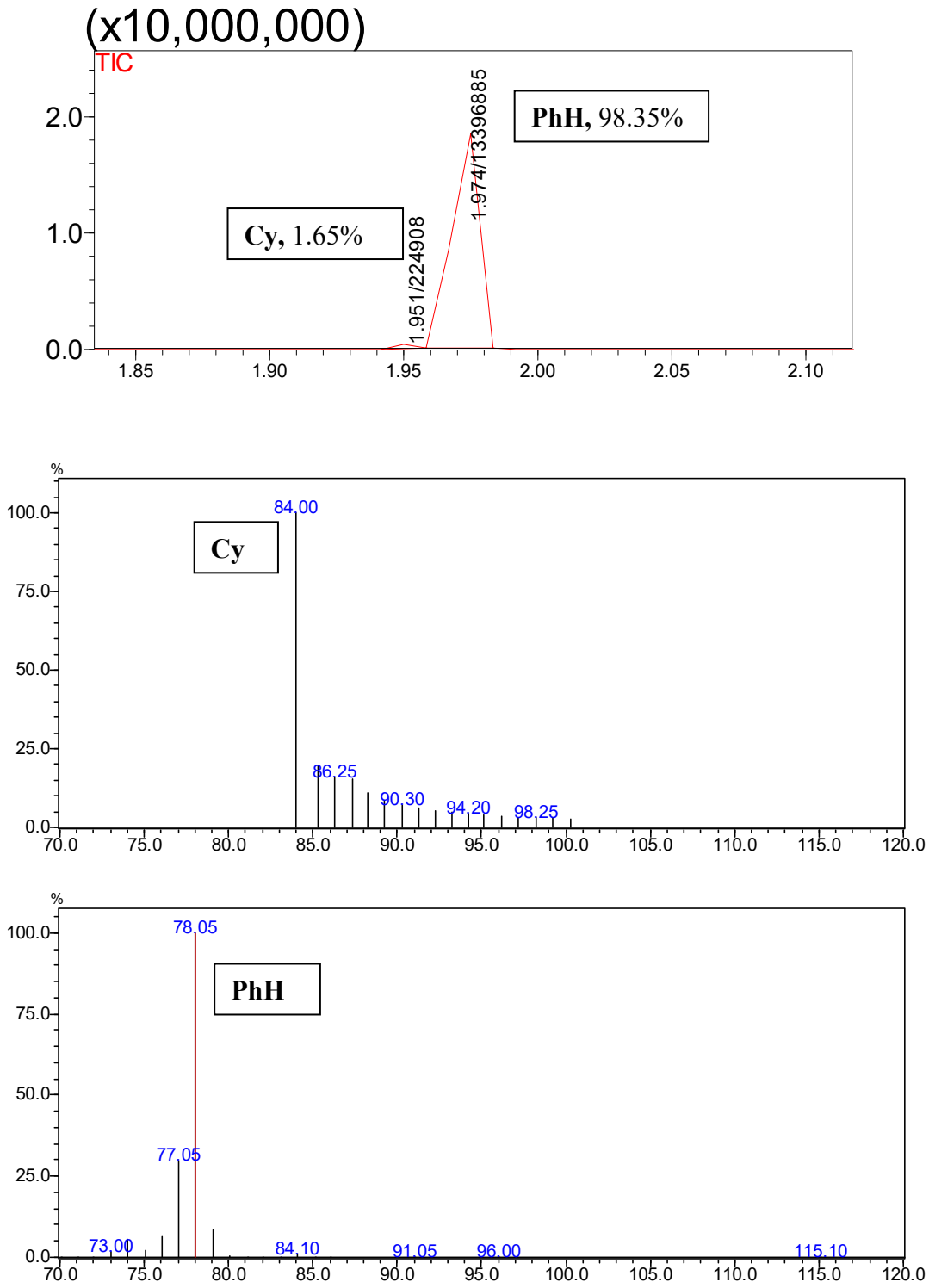
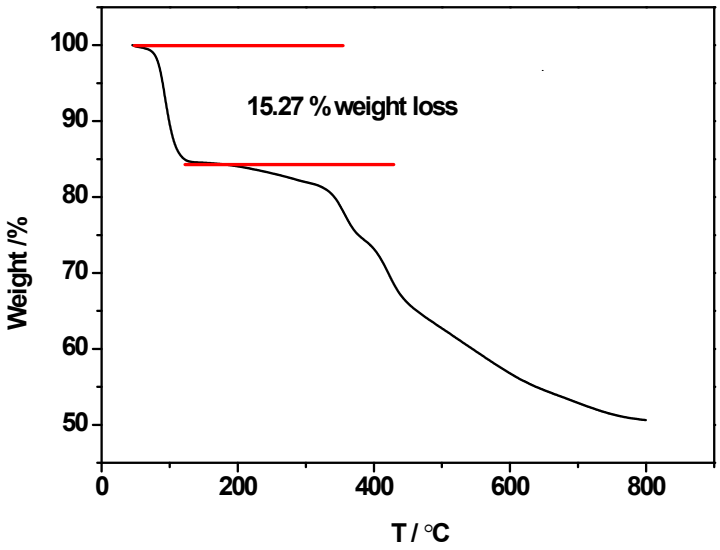


Figure S17. Relative uptakes of **PhH** and **Cy** adsorbed in **1** for 6 h and then placed at room temperature for 4 hours using head space gas chromatography.



1	15.3%
2	15.5%
3	15.3%
average	15.37%
error	0.094

Figure S18. Thermogravimetric analysis of **1** after sorption of **PhH** and **Cy** adsorbe vapor for 6 h and then placed at room temperature for 4 hours. The weight loss from 55 to 127 °C corresponded to the release of 2.21 **PhH** molecules per **1**.

7. Recyclability of 1

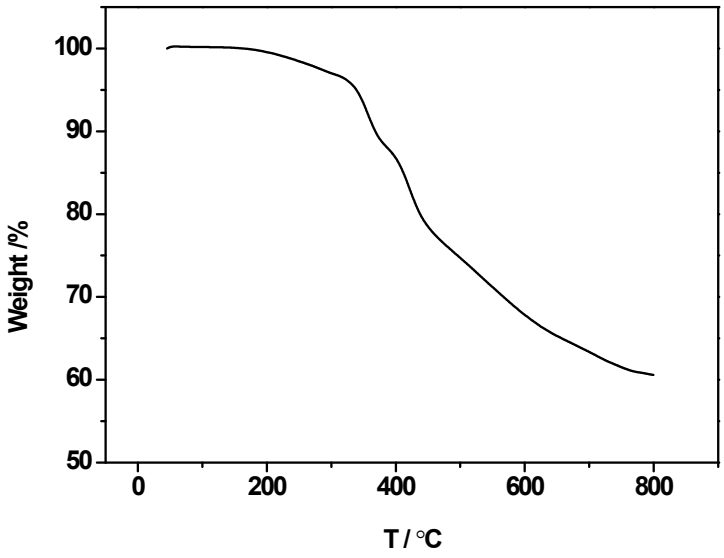


Figure S19. Thermogravimetric analysis of **1** after sorption of **PhH** and **Cy** then heating at 100 °C under vacuum for 2 h.

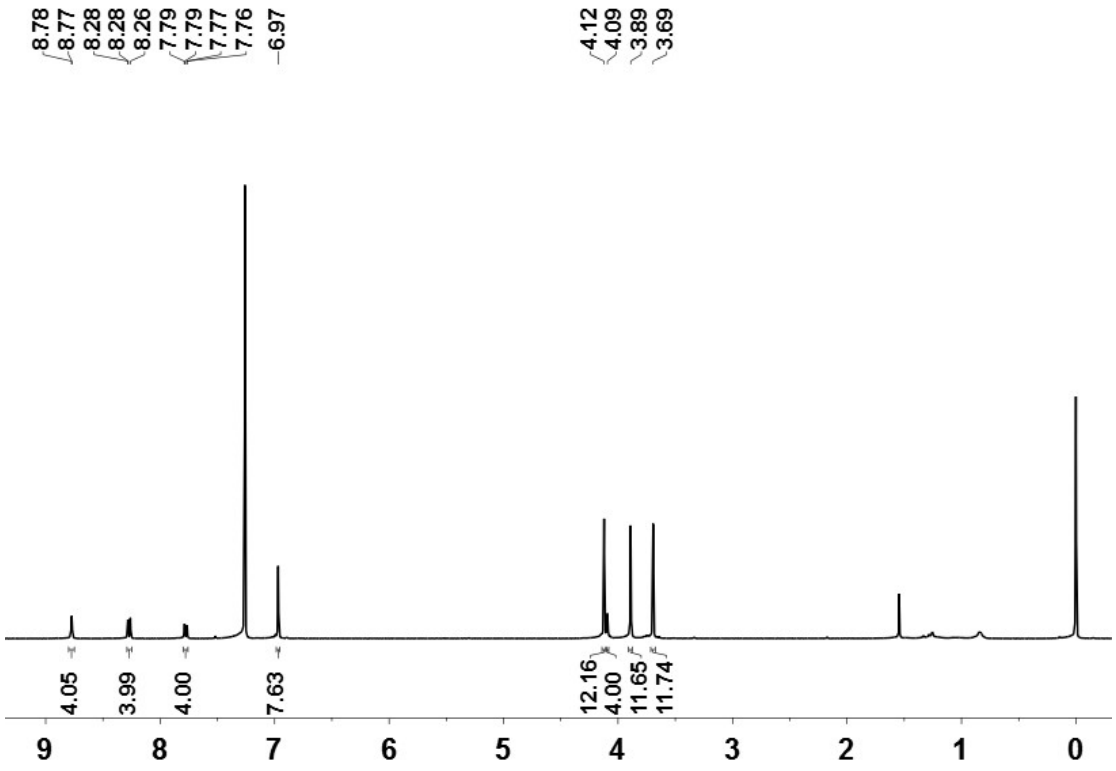


Figure S20. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **1** after sorption of **PhH** and **Cy** then heating at 100 °C under vacuum for 2 h.

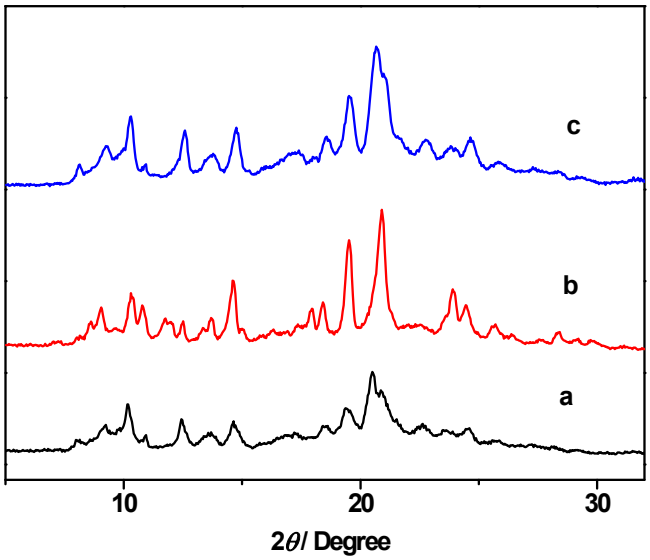


Figure S21. Powder X-ray diffraction patterns of **1**: (a) original activated **1**; (b) **1** after sorption of **PhH** and **Cy** then heating at 100 °C under vacuum for 2 h; (c) **1** after 7 cycles.

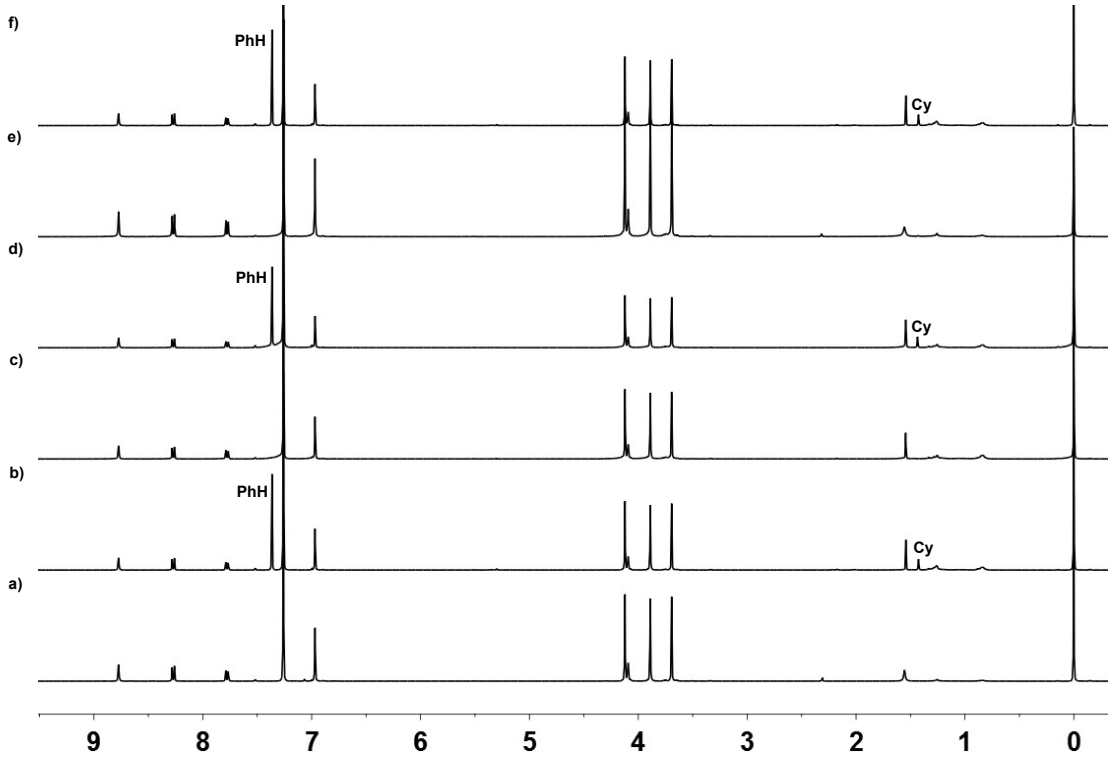


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of (a) original activated **1**; (b) **a** after sorption of **PhH** and **Cy** for 6 h and then placed at room temperature for 4 hours; (c) heating **b** at 100 °C under vacuum for 2 h; (d) c after sorption of **PhH** and

Cy for 6 h and then placed at room temperature for 4 hours; (e) heating **d** at 100 °C under vacuum for 2 h; (f) **e** after sorption of **PhH** and **Cy** for 6 h and then placed at room temperature for 4 hours.

8. Crystal data for 1@PhH_4

Identification code	CCQ-100K
Empirical formula	$C_{90}H_{84}O_{12}$
Formula weight	1357.57
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	15.3431(2)
b/Å	15.1750(2)
c/Å	31.1888(5)
α/°	90
β/°	100.9470(10)
γ/°	90
Volume/$Å^3$	7129.60(18)
Z	4
$\rho_{calc}g/cm^3$	1.265
μ/mm^{-1}	0.662
F(000)	2880.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.772 to 152.17
Index ranges	$-15 \leq h \leq 19$, $-18 \leq k \leq 19$, $-39 \leq l \leq 38$
Reflections collected	21051
Independent reflections	7156 [R_{int} = 0.0251, R_{sigma} = 0.0268]
Data/restraints/parameters	7156/0/466
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0468, wR_2 = 0.1326
Final R indexes [all data]	R_1 = 0.0543, wR_2 = 0.1377
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.30

9. References

SI. B. V. Phulwale, S. K. Mishra, M. Nečas and C. Mazal, Phenanthrylene-butadiynylene and phenanthrylenethienylene macrocycles. Synthesis, structure and properties, *J. Org. Chem.,* 2016, **81**, 6244.