Electronic Supplementary Information

Adsorptive separation of *para*-xylene by nonporous adaptive crystals of

Phenanthrene[2]arene

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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. Activated host **1** was prepared by recrystallization in the mixture of CH_2Cl_2/MeOH and dried under vacuum at 150 °C for 6 h. 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). The GC method was described below: the oven was programmed to heat up from 40 °C to 220 °C with an increments of 10 °C/min with 10 min hold, resulting 38 min run time in total; the injection temperature was 250 °C; the detection temperature was 330 °C with hydrogen, air, and make-up flow-rates of 40, 400, and 30 mL/min respectively; helium (carrier gas) flow-rate 2.1 mL/min. The samples were injected in the split mode (20:1). Numeric integration of the resulting peaks was performed using the

supplied ACD/ChemSketch and AI software package.

2. Synthesis of New compounds.
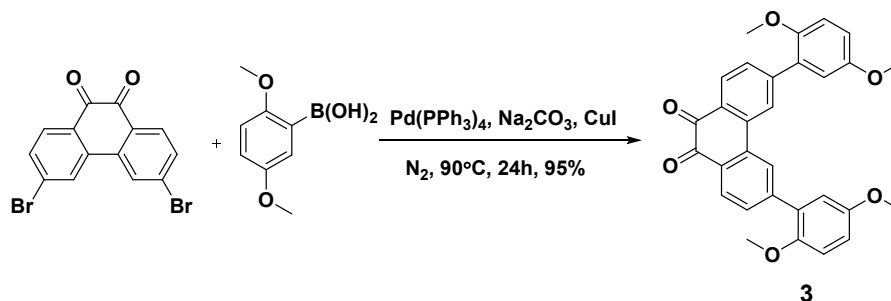
Compound 3 A mixture of 3,6-dibromophenanthrene-9,10-dione (3.64 g, 10 mmol), Na_2CO_3 (2.96 g, 28 mmol), 2,5-dimethoxyphenylboronic acid (4.00 g, 22 mmol) and tetrakis(triphenylphosphine)palladium (0.48 g, 0.42 mmol) in 100 mL dioxane and water (v/v = 5:1) in a flask was stirred at 90 °C for 24 h under N_2. After being cooled to room temperature, the reaction mixture was poured into water, and the resulting red precipitate was washed with water and then dried under a vacuum to afford compound **2** (4.56 g, yield 95%) as a red solid. M.p.: 225-227 °C. ^1H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, J = 8.0 Hz, 2H), 8.15 (s, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.00 – 6.89 (m, 6H), 3.80 (d, J = 15.5 Hz, 12H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 180.29, 153.88, 150.77, 146.50, 135.76, 130.65, 130.29, 129.92, 129.63, 125.28, 116.39, 114.56, 112.85, 56.35, 55.89. HRMS (APCI) m/z: [M+H]$^+$ calcd for $C_{30}H_{25}O_6$, 481.1651; found, 481.1654.
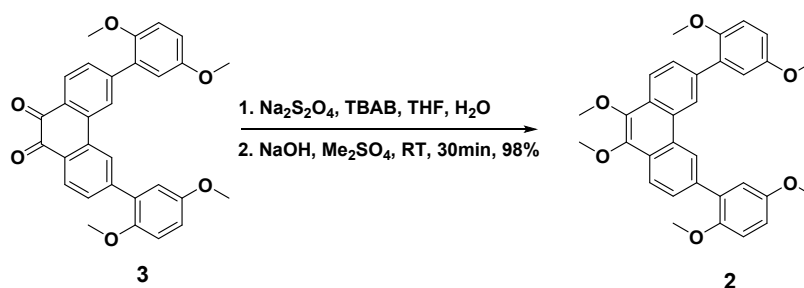
Compound 2 Bu$_4$NBr (0.38 g, 1.2 mmol), compound **3** (1.44 g, 3.0 mmol), and $Na_2S_2O_4$ (4.08 g, 12 mmol) were suspended in aqueous THF (1:1, 50 mL) and stirred until the reaction mixture was homogeneous. Me$_2$SO$_4$ (2 mL) was slowly added, followed by a concentrated aq. NaOH solution (14 M, 5 mL). After stirring for 5 min,

ice (20 g) was slowly added over 5 min and the mixture was further stirred for 20 min. The resulting solid was filtered and dissolved in EtOAc (50 mL). The solution was washed with water (3 × 100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo to afford the title compound **2** as white crystals (1.50 g, 98%). All data are consistent with the previous results that published by our group. ^{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.

3. ^{1}H NMR and ^{13}C NMR Spectral of New compounds.
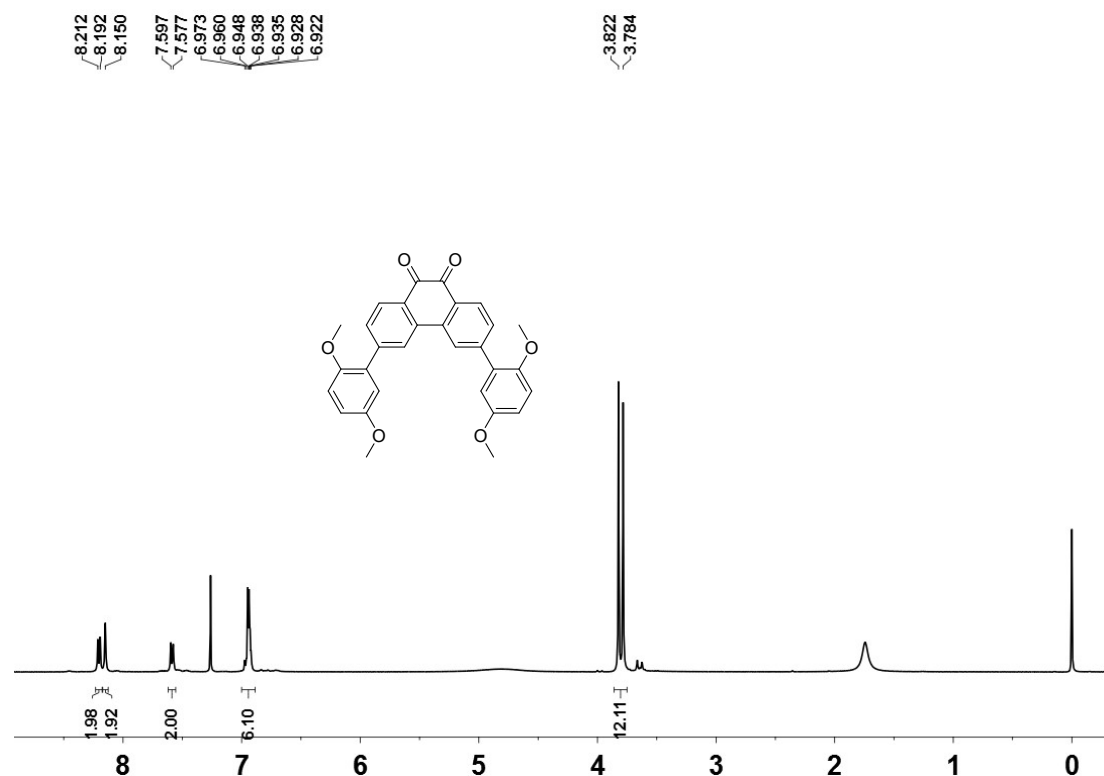
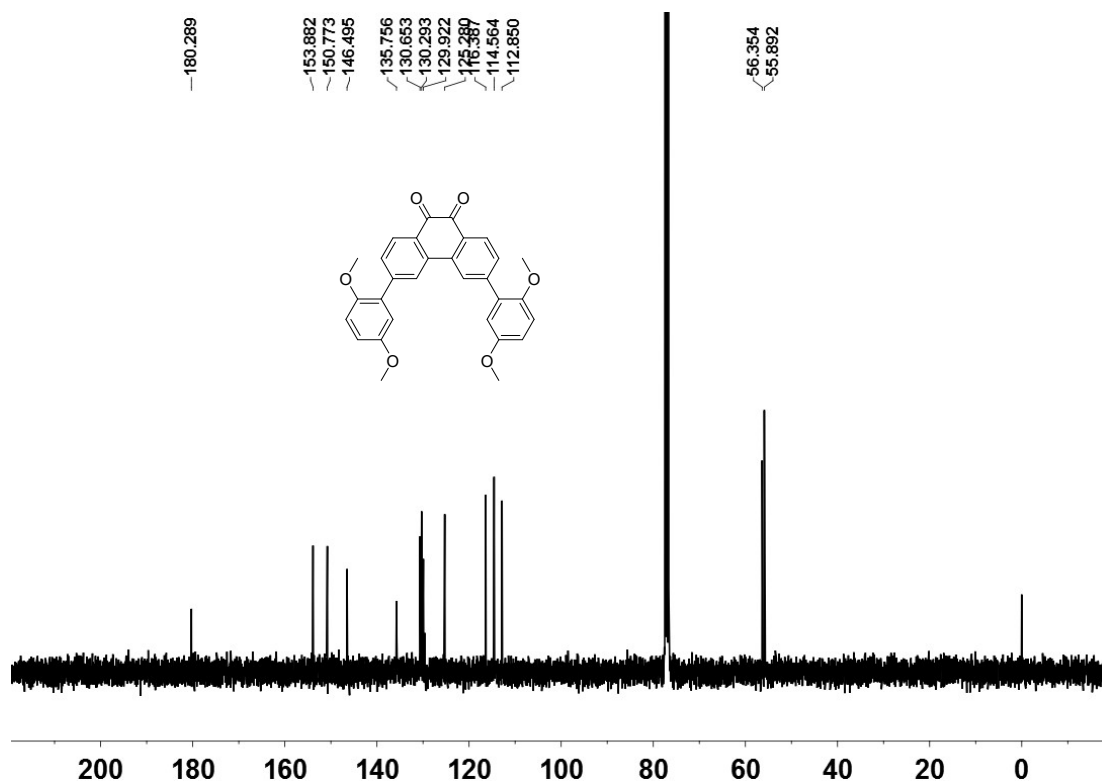**Figure S1.**^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **3**

Figure S2. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298K) of **3**

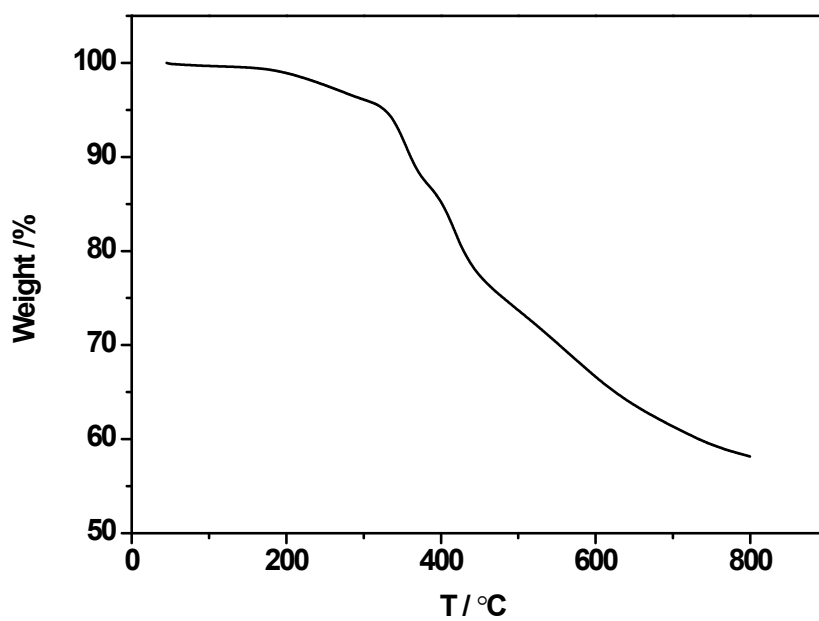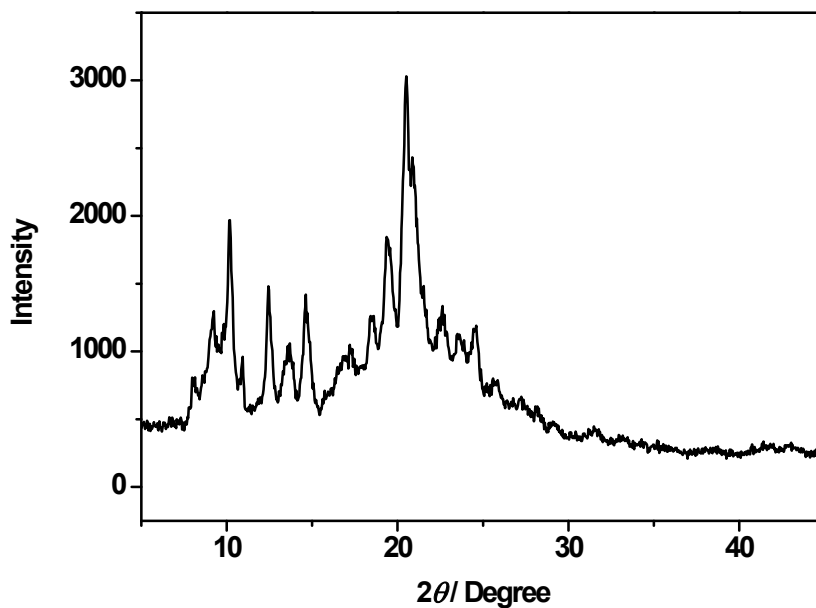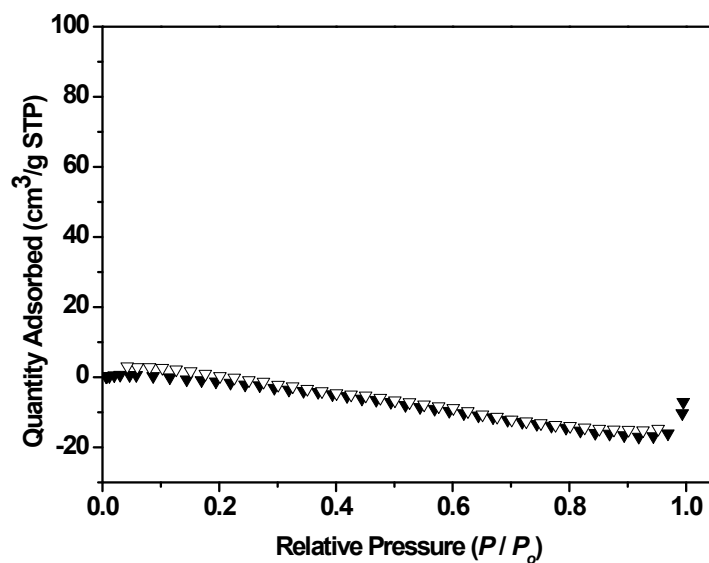## 4. Characterization of Activated 1 Crystals

**Figure S3.** Thermogravimetric analysis of **1**

**Figure S4.** Powder X-ray diffraction pattern of **1**.

Figure S5. N2 adsorption isotherm of **1**. The BET surface area value is 4.9971 m^2/g. Adsorption, closed symbols; desorption, open symbols.

## 5. Single-Component *p*X/*m*X Adsorption Experiments

^{1}H NMR experiments were performed by dissolving **1** after vapor sorption in CDCl$_3$. TGA profiles were recorded using **1** after vapor sorption.
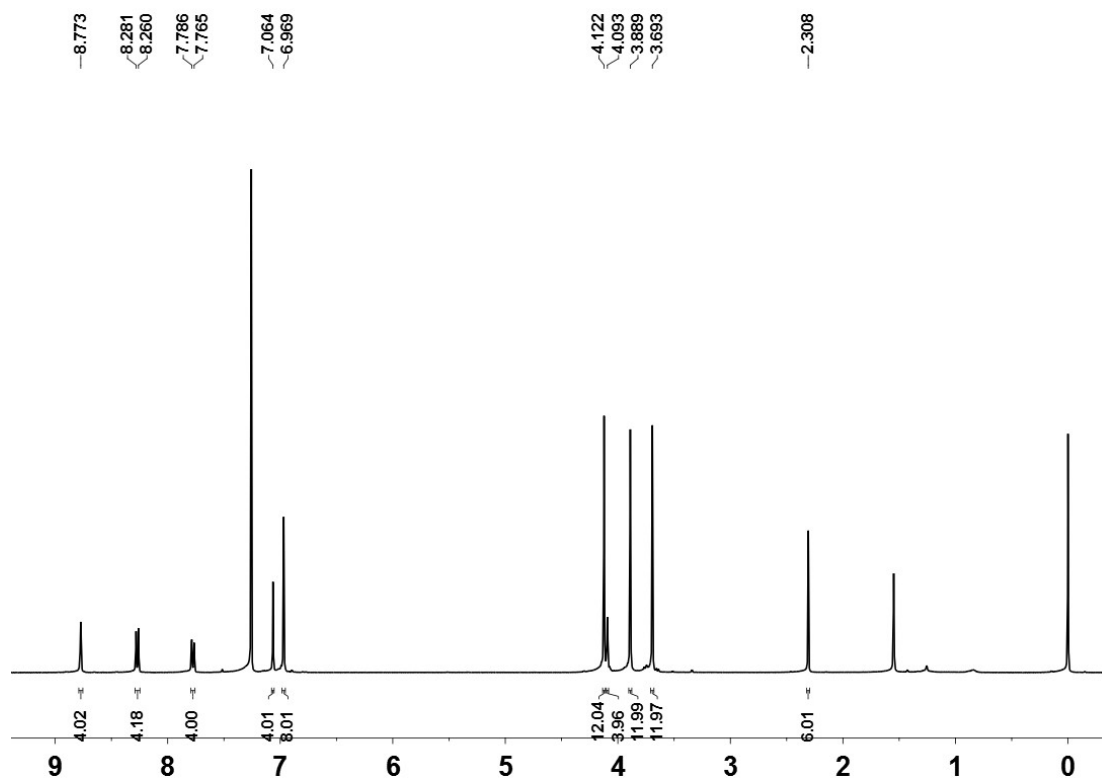
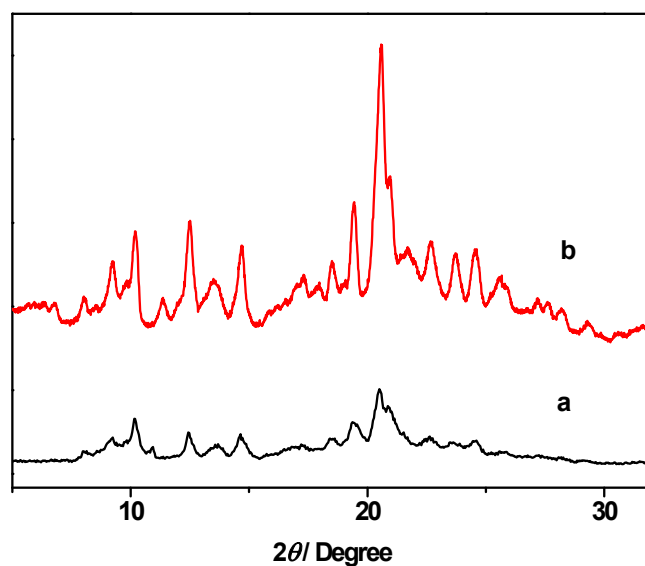**Figure S6.** ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 293 K) of activated **1** after sorption of **p**X vapor for 20 h.
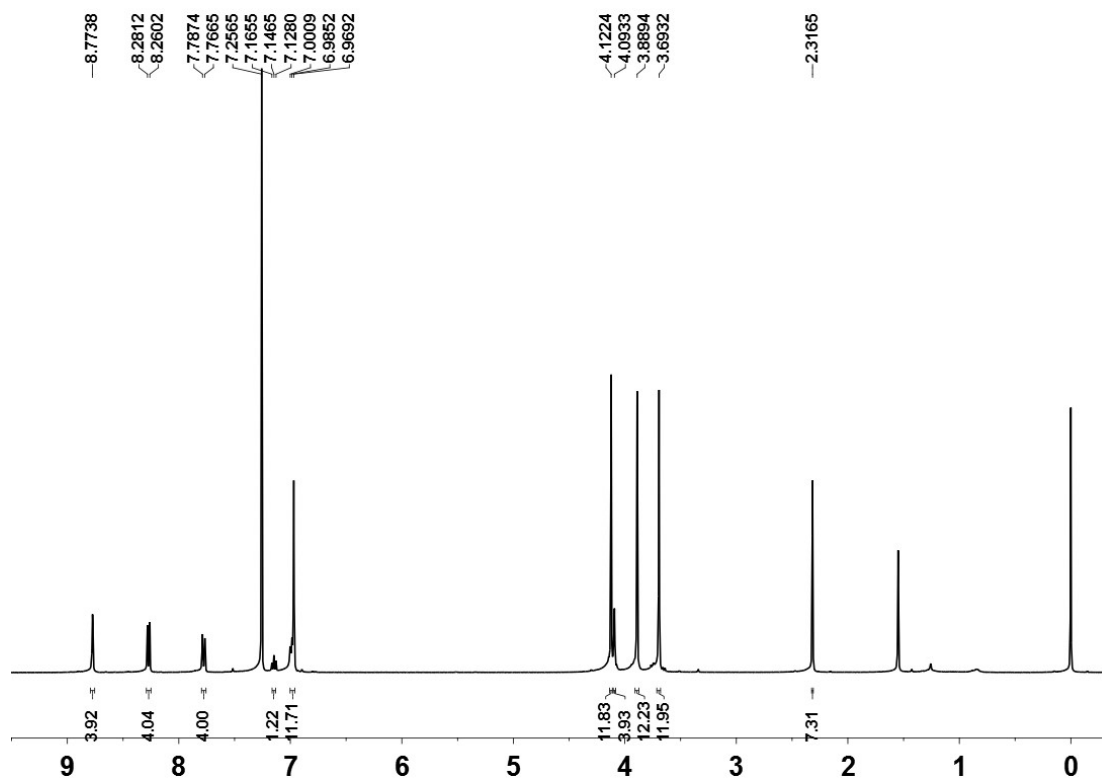
Figure S7. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 293 K) of activated **1** after sorption of **m**X vapor for 20 h.
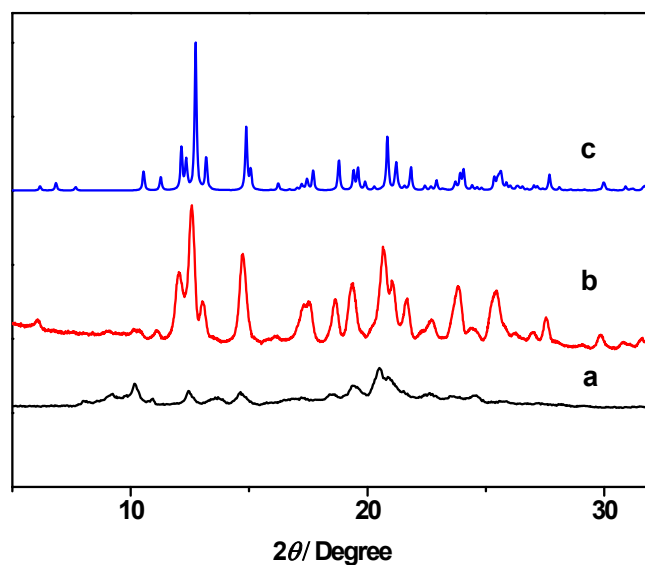
Figure S8. PXRD patterns of **1**: (a) original activated **1**; (b) after adsorption of **pX** vapor; (c) simulated from single crystal structure of **1@pX**.


Figure S9. PXRD patterns of **1**: (a) original activated **1**; (b) after adsorption of **mX** vapor.

## 6. Uptake from a **pX**/**mX** 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 **pX**/**mX** mixture. Uptake by **1** was

measured hour by hour by completely dissolving the crystals and measuring the ratio of *pX* or *mX* to **1** by ^{1}H NMR. The relative uptakes of *pX* and *mX* by **1** 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.
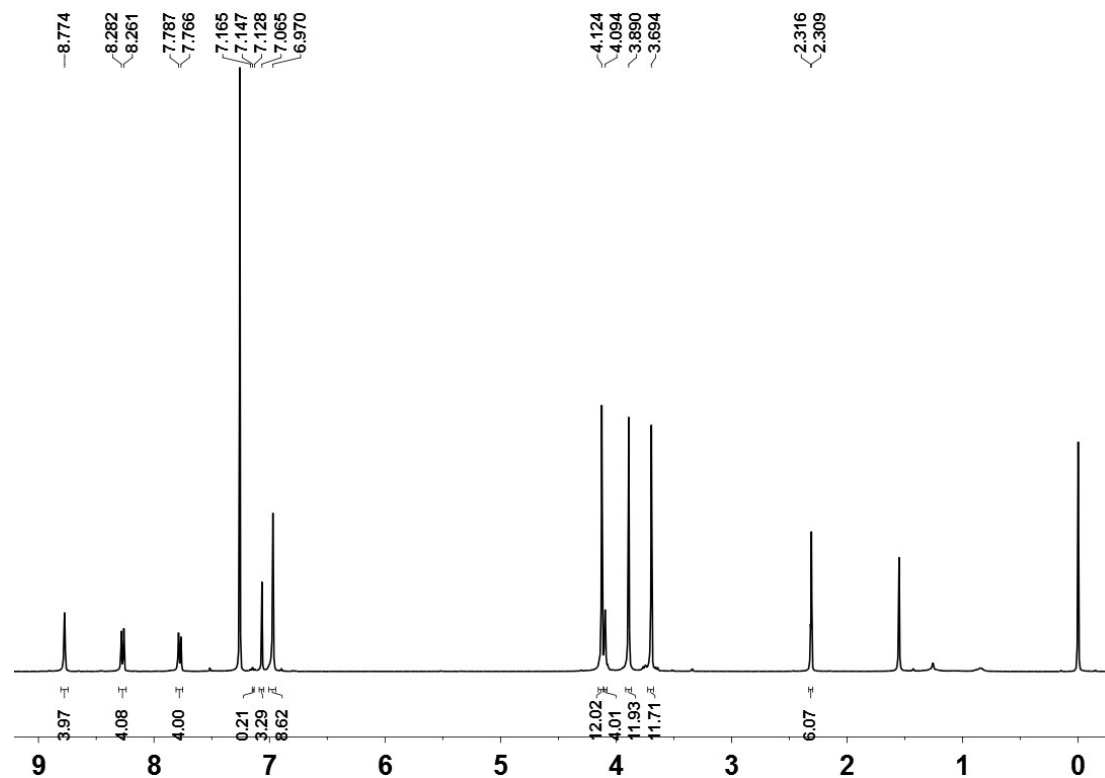
Figure S10. ^{1}H NMR spectrum (400 MHz, CDCl₃, 293 K) of **1** after sorption of an equimolar *pX/mX* mixture vapor for 20 h.
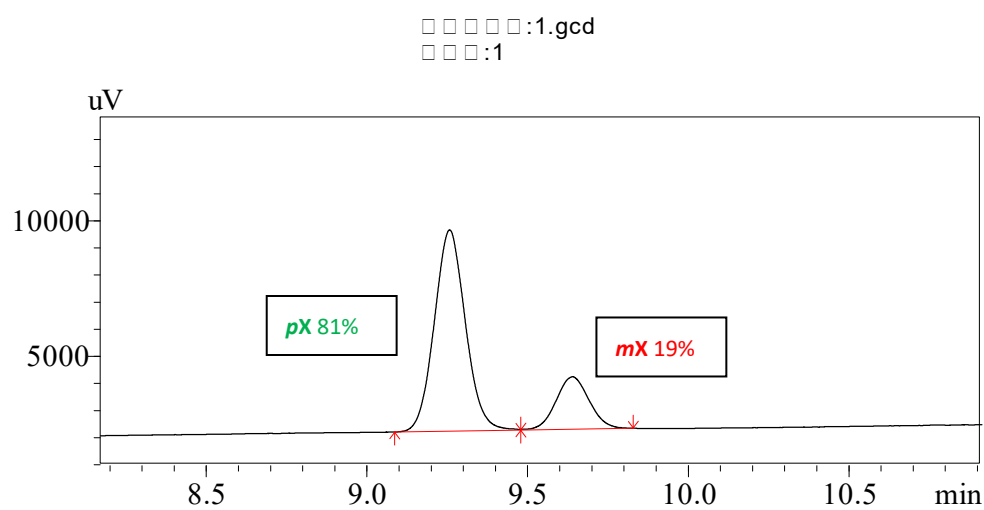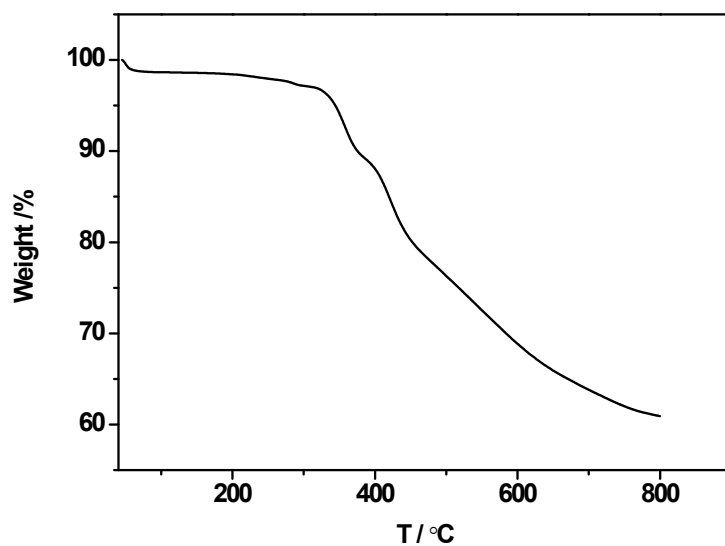

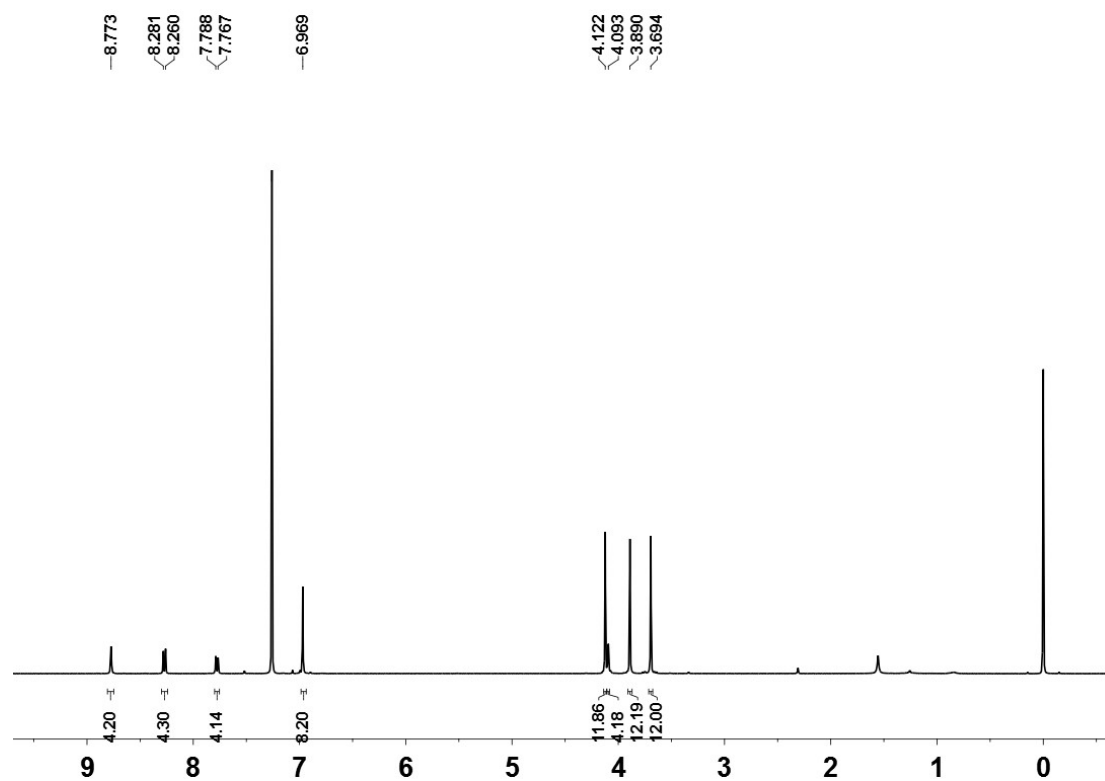**Figure S11.** Relative uptakes of *pX* and *mX* adsorbed in **1** for 20 h using head space gas chromatography.
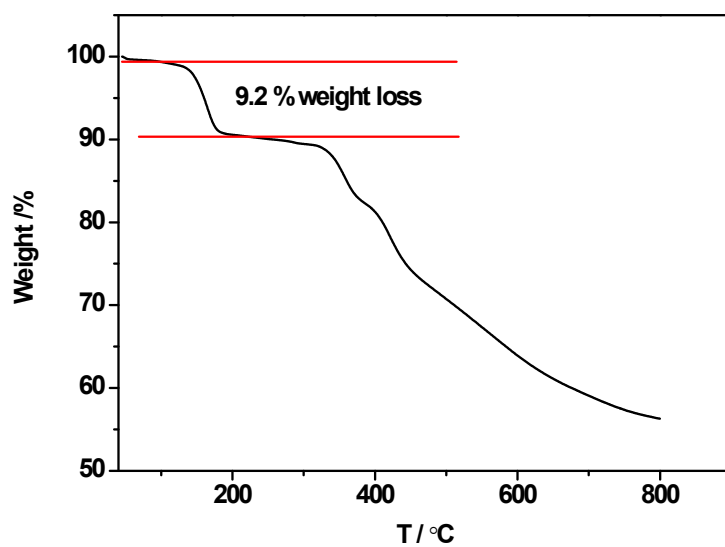
Figure S12. Thermogravimetric analysis of **1** after sorption of *p*X and *m*X adsorbe vapor for 20 h.

7. Recyclability of 1

Figure S13. Thermogravimetric analysis of **1** after sorption of *p*X and *m*X then heating at 150 °C under vacuum for 3 h.

Figure S14. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 293 K) of **1** after sorption of **pX** and **mX** then heating at 150 °C under vacuum for 3 h.
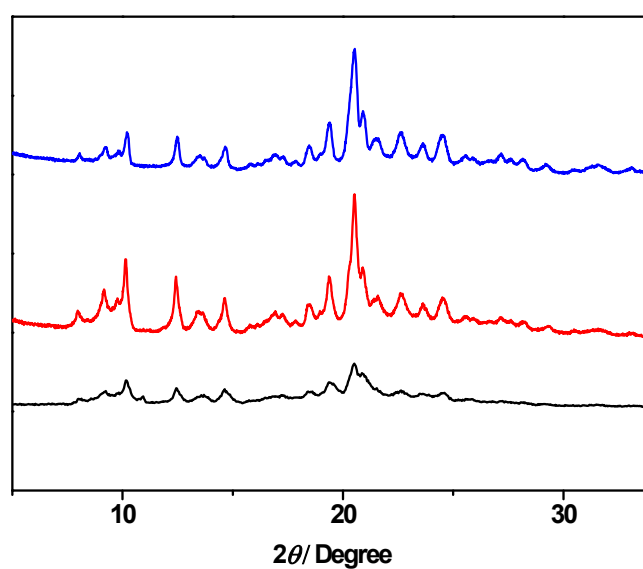
Figure S15. Powder X-ray diffraction patterns of **1**: (a) original activated **1**; (b) **1** after sorption of **pX** and **mX** then heating at 150 °C under vacuum for 3 h; (c) **1** after 7 cycles.
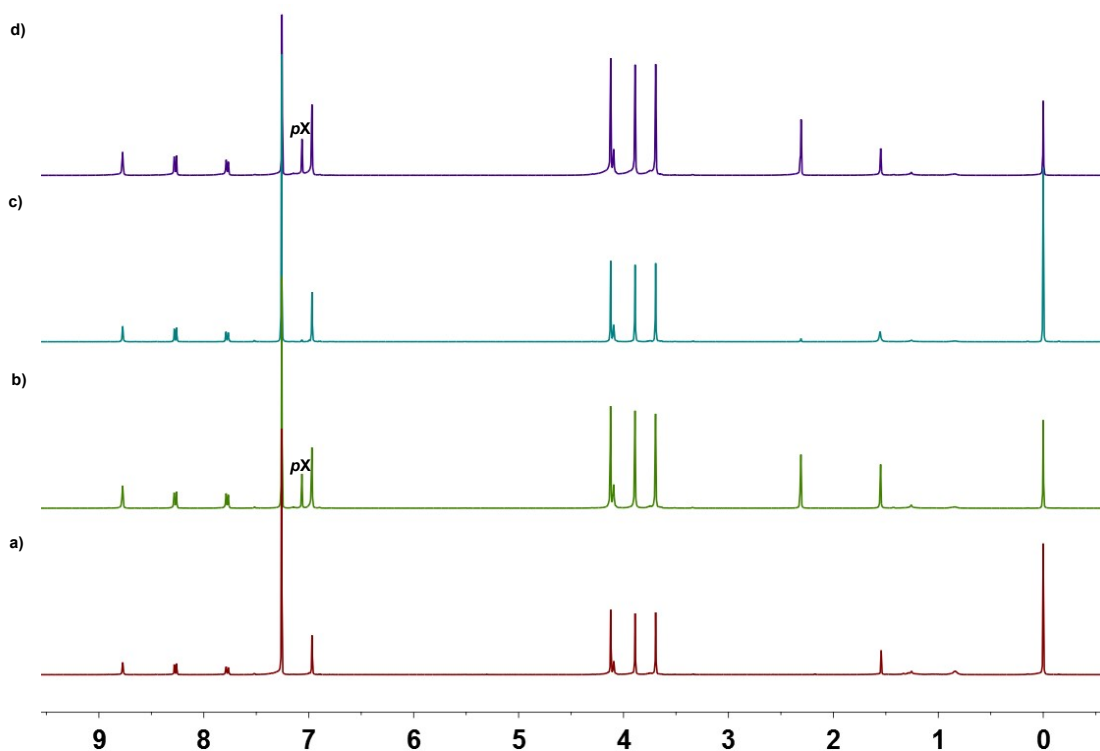
Figure S16. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298K) of (a) original **1**; (b) **1** after adsorption of **p**X/**m**X mixture vapor; (c) **p**X loaded **1** crystals after removal of **p**X; (d) desolvated **p**X loaded **1** crystals after adsorption of **p**X/**m**X mixture vapor.

8. Crystal data for 1@*p*X and 1@2*m*X

1@*p*X

Identification code	22022501_0m_a
Empirical formula	C$_{74}$H$_{70}$O$_{12}$
Formula weight	1151.30
Temperature/K	300.00
Crystal system	monoclinic
Space group	P2$_1$/n
a/Å	15.047(4)
b/Å	8.2362(19)
c/Å	26.661(6)
α/°	90
β/°	104.502(3)
γ/°	90
Volume/Å^3	3198.7(13)
Z	2
ρ$_{calc}$g/cm^3	1.195

μ/mm^{-1}	0.080
F(000)	1220.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.846 to 54.932
Index ranges	-19 ≤ h ≤ 19, -10 ≤ k ≤ 10, -34 ≤ l ≤ 33
Reflections collected	34096
Independent reflections	7226 [R_{int} = 0.0355, R_{sigma} = 0.0303]
Data/restraints/parameters	7226/850/569
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0627, wR_2 = 0.1826
Final R indexes [all data]	R_1 = 0.0899, wR_2 = 0.2054
Largest diff. peak/hole / e Å^{-3}	0.42/-0.41

1@2*m*X

Table 1 Crystal data and structure refinement for 33.

Identification code	33
Empirical formula	$C_{82}H_{80}O_{12}$
Formula weight	1257.46
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.879(5)
b/Å	12.427(4)
c/Å	19.765(7)
α/°	90
β/°	93.893(5)
γ/°	90
Volume/Å^3	3401.3(19)
Z	2
ρ_{calc}g/cm^3	1.228
μ/mm^{-1}	0.081
F(000)	1336.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.478 to 55.192
Index ranges	-18 ≤ h ≤ 18, -16 ≤ k ≤ 15, -25 ≤ l ≤ 25
Reflections collected	37527
Independent reflections	7753 [R_{int} = 0.0952, R_{sigma} = 0.0959]
Data/restraints/parameters	7753/0/432
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0691, wR_2 = 0.1704
Final R indexes [all data]	R_1 = 0.1630, wR_2 = 0.2268
Largest diff. peak/hole / e Å^{-3}	0.25/-0.24

9. Adsorption kinetic analysis using three models

$$n_t = k_p t^{0.5} + C$$ (eq. S3) where k_p is the rate constant for intra-particle diffusion.

$$n_t = n_{eq} - n_{eq}e^{-k_1 t}$$ (eq. S4) where k_1 is the rate constant for pseudo-first-order adsorption.

$$n_t = \frac{1}{1-k_2 n_{eq}^2 t} - 1$$ (eq. S5) where k_2 is the rate constant for pseudo-second-order adsorption

n_{eq} and n_t represent the amount of adsorbate adsorbed per amount of adsorbent determined at equilibrium and time *t*, respectively.

The data did not fit well with either PFO or PSO, indicating the experimental

conditions (e.g., the concentration of *p*X and *m*X and the dosage of NAC) did not meet the extreme conditions where the initial adsorbate concentration to the adsorbent maximum capacity should be higher than a threshold
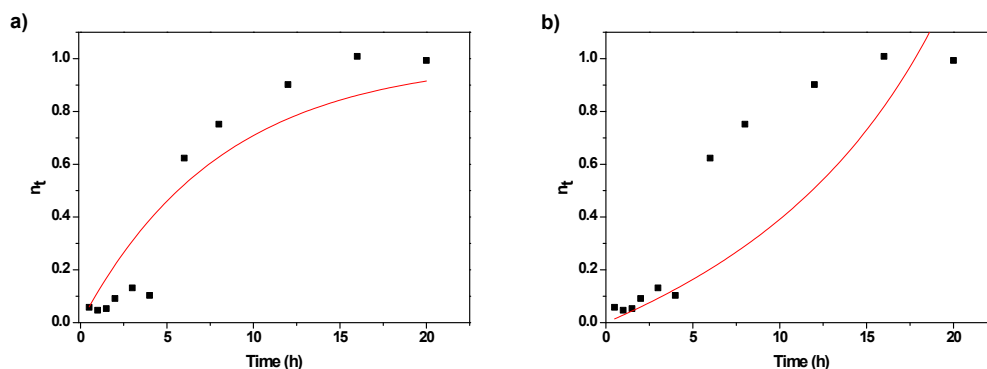
Figure S17. The adsorption kinetics data of *p*X vapor onto **1** were fitted with (a) PFO models, and (b) PSO models. (IPD models cannot fit)
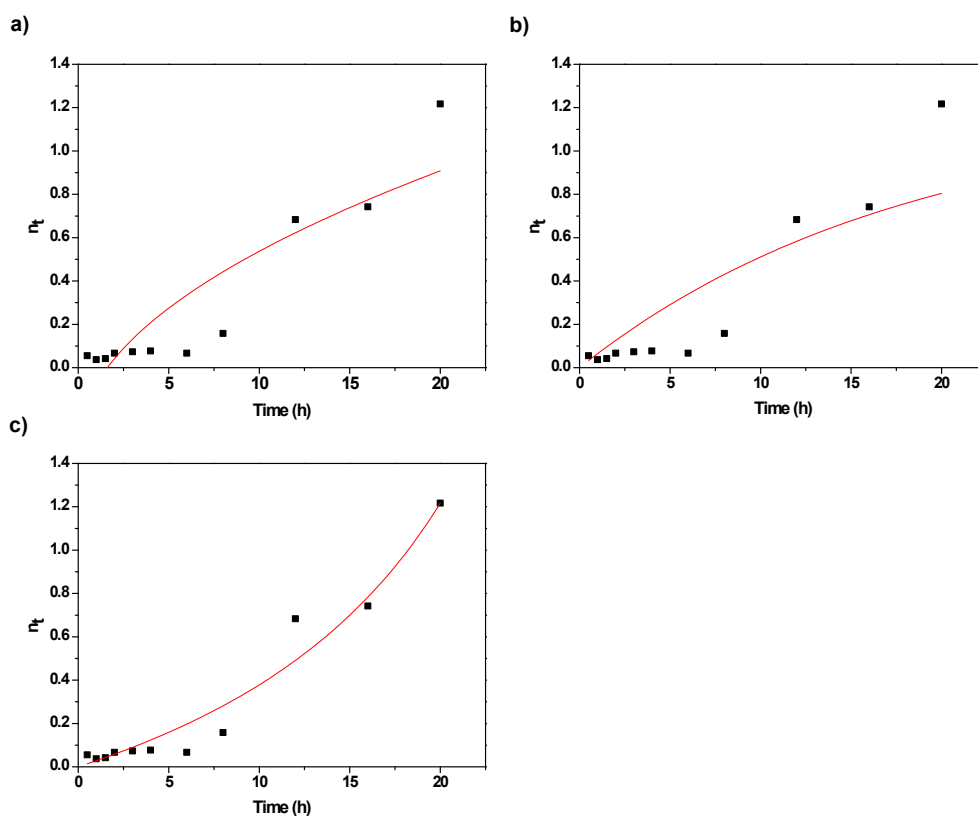
Figure S18. The adsorption kinetics data of *m*X vapor onto **1** were fitted with (a) IPD models, (b) PFO models, and (c) PSO models.