Electronic Supplementary Information

Adsorptive separation of picoline isomers by adaptive calix[3]acridan crystals

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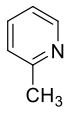
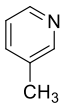
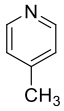
1. Materials and methods

1.1 Materials

All the reagents including 2-picoline (**2-MP**), 3-picoline (**3-MP**) and 4-picoline (**4-MP**) were commercially available and used without further purification. Calix[3]acridan (**C[3]A**) was synthesized according to previously reported procedures. Activated crystalline **C[3]A,** referred to as **C[3]Aα**, was initially recrystallized from acetone, and then dried under vacuum at 80 °C for 24 hours.

Table S1. Physical properties of **2-MP**, **3-MP** and **4-MP**.

Picoline isomers	**2-MP**	**3-MP**	**4-MP**
Structural formula			
Melting point (°C)	-70	-18	2.4
Boiling point (°C)	128	143	144
Saturated Vapor pressure at 298K (kPa)	1.2	0.6	0.76

1.2 Methods

Solution NMR spectroscopy. NMR spectroscopy experiments were recorded on the Bruker Avance III 400 MHz NMR spectrometer.

Single-crystal X-ray diffraction. Single-crystal X-ray diffraction data were recorded on a XtaLAB Synergy-R X-ray diffractometer at 170 K.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) patterns were recorded on an Empyrean X-ray diffractometer. Data were collected over the range of 5−45° in 5°/min steps.

BET surface area measurement. Brunauer-Emmett-Teller (BET) surface area measurement was performed on a Quantachrome Autosorb-iQ-C analyzer. Samples were degassed under dynamic vacuum for 12 h at 200 °C before each measurement. N_2 isotherms were measured using a liquid nitrogen bath (77 K).

Thermogravimetric analysis. Thermogravimetric analysis (TGA) was taken with TGA 8000 operated at 10 K/min at nitrogen atmosphere.

Gas chromatography. Gas chromatography (GC) measurements were performed on an Agilent 7890B with an FID detector and a 2,3-diO-acetyl-6-0-TBDMS-β-cyclodextrin capillary column (Supelco Beta DEX 225; 30 mm × 0.25 mm × 0.25 μm). The following GC method was used: the oven was programmed from 50 °C, ramped at 2 °C/min increments to 100 °C with 15 min hold; injection temperature 250 °C; detection temperature 280 °C with nitrogen, air, and make-up flow-rates of 25, 400, and 30 mL/min, respectively; helium (carrier gas) flow-rate 2.0 mL/min.

Solid-vapor adsorption experiments. In a typical solid-vapor picoline isomers adsorption experiment, an open vial (3 mL) containing 20 mg of activated guest-free **C[3]A** crystals was placed into a sealed vial (20 mL) containing 1 mL of **2-MP**, **3-MP**, **4-MP** (single-component adsorption), 1:1 mixture of binary mixture of picoline isomers (two-component adsorption) and 1:1:1 mixture ternary mixture of picoline isomers (three-component adsorption). The adsorption process was monitored over time by completely dissolving a portion of the crystals in $CDCl_3$ and measuring ^1H NMR spectra. The relative uptake amount of picoline isomers was determined by heating the crystals to release the adsorbed vapor using gas chromatography. Before measurement, the crystals were heated at 50 °C for 30 minutes to remove the surface-physically adsorbed vapor.

2. Crystal structures and crystal data

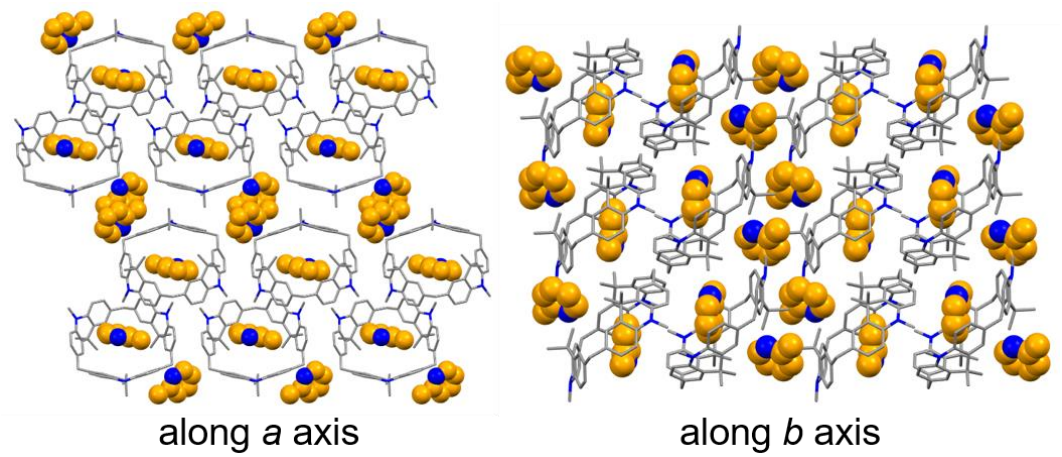


Fig. S1 Packing mode in the single-crystal structure of 2(**2-MP**)@**C[3]A**.

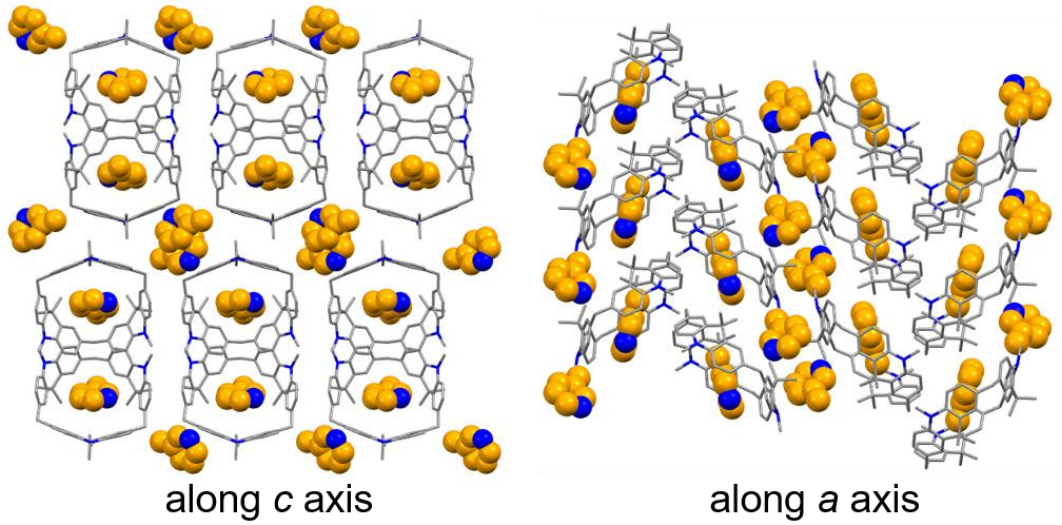


Fig. S2 Packing mode in the single-crystal structure of 2(**3-MP**)@**C[3]A**.

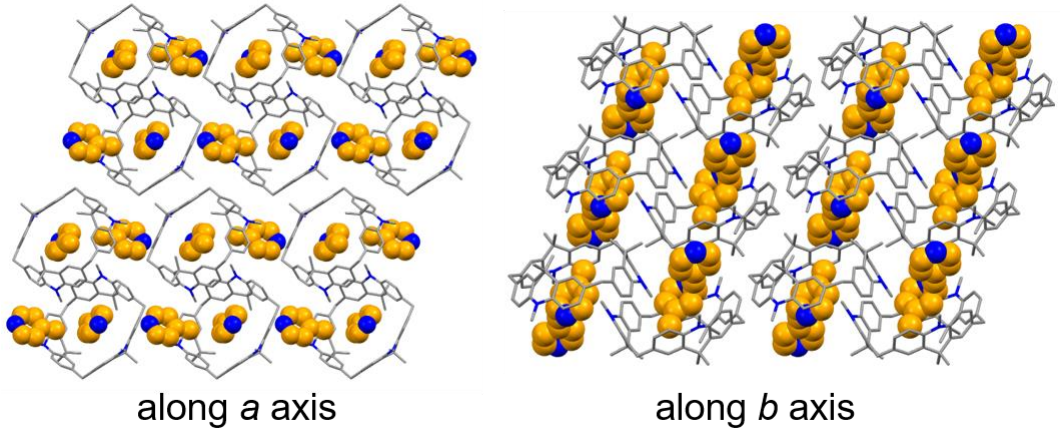


Fig. S3 Packing mode in the single-crystal structure of 2(**4-MP**)@**C[3]A**.

Table S2. Crystal data and structure refinement parameters for 2(**2-Mp**)@**C[3]A**.

Compound	2(**2-Mp**)@**C[3]A**
CCDC No.	2107535
Empirical formula	$C_{63}H_{65}N_5$
Formula weight	892.20
Temperature/K	169.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.27290(10)
b/Å	13.6876(3)
c/Å	20.4931(4)
α/°	73.661(2)
β/°	82.2150(10)
γ/°	84.642(2)
Volume/Å^3	2468.83(8)
Z	2
ρ_{calc}g/cm^3	1.200
μ/mm^{-1}	0.532
F(000)	956.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.522 to 150.598
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 16$, $-25 \leq l \leq 25$
Reflections collected	32982
Independent reflections	9747 [R_{int} = 0.0160, R_{sigma} = 0.0138]
Data/restraints/parameters	9747/0/624
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0489, wR_2 = 0.1291
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1305
Largest diff. peak/hole / e Å^{-3}	0.65/-0.39
Crystallization solvents	2-picoline

Table S3. Crystal data and structure refinement parameters for 2(**3-Mp**)@**C[3]A**.

Compound	2(**3-Mp**)@**C[3]A**
CCDC No.	2107531
Empirical formula	$C_{63}H_{65}N_5$
Formula weight	888.20
Temperature/K	169.97(12)
Crystal system	monoclinic

Space group	$P2_1/c$
a/Å	13.18180(10)
b/Å	39.3842(4)
c/Å	9.47760(10)
α/°	90
β/°	98.4260(10)
γ/°	90
Volume/Å^3	4867.23(8)
Z	4
ρ_{calc}g/cm^3	1.212
μ/mm^{-1}	0.526
F(000)	1904.0
Crystal size/mm^3	0.4 × 0.25 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.488 to 150.506
Index ranges	$-14 \leq h \leq 16$, $-48 \leq k \leq 48$, $-11 \leq l \leq 11$
Reflections collected	45750
Independent reflections	9670 [R_{int} = 0.0349, R_{sigma} = 0.0284]
Data/restraints/parameters	9670/0/624
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0426, wR_2 = 0.1089
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1117
Largest diff. peak/hole / e Å^{-3}	0.22/-0.23
Crystallization solvents	3-picoline

Table S4. Crystal data and structure refinement parameters for 2(**4-Mp**)@**C[3]A**.

Compound	2(**4-Mp**)@**C[3]A**
CCDC No.	2107534
Empirical formula	$C_{63}H_{65}N_5$
Formula weight	886.20
Temperature/K	169.99(11)
Crystal system	triclinic
Space group	P-1
a/Å	9.6062(2)
b/Å	14.1110(3)
c/Å	20.1126(3)
α/°	102.6520(10)
β/°	103.668(2)
γ/°	104.100(2)
Volume/Å^3	2456.15(9)

Z	2
ρ_{calc}g/cm^3	1.198
μ/mm^{-1}	0.515
F(000)	950.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.73 to 150.498
Index ranges	-11 ≤ h ≤ 10, -17 ≤ k ≤ 17, -25 ≤ l ≤ 25
Reflections collected	30441
Independent reflections	9645 [R_{int} = 0.1296, R_{sigma} = 0.0919]
Data/restraints/parameters	9645/0/624
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0883, wR_2 = 0.1666
Final R indexes [all data]	R_1 = 0.1147, wR_2 = 0.1757
Largest diff. peak/hole / e Å^{-3}	0.34/-0.28
Crystallization solvents	4-picoline

3. Characterization of activated calix[3]acridan crystals

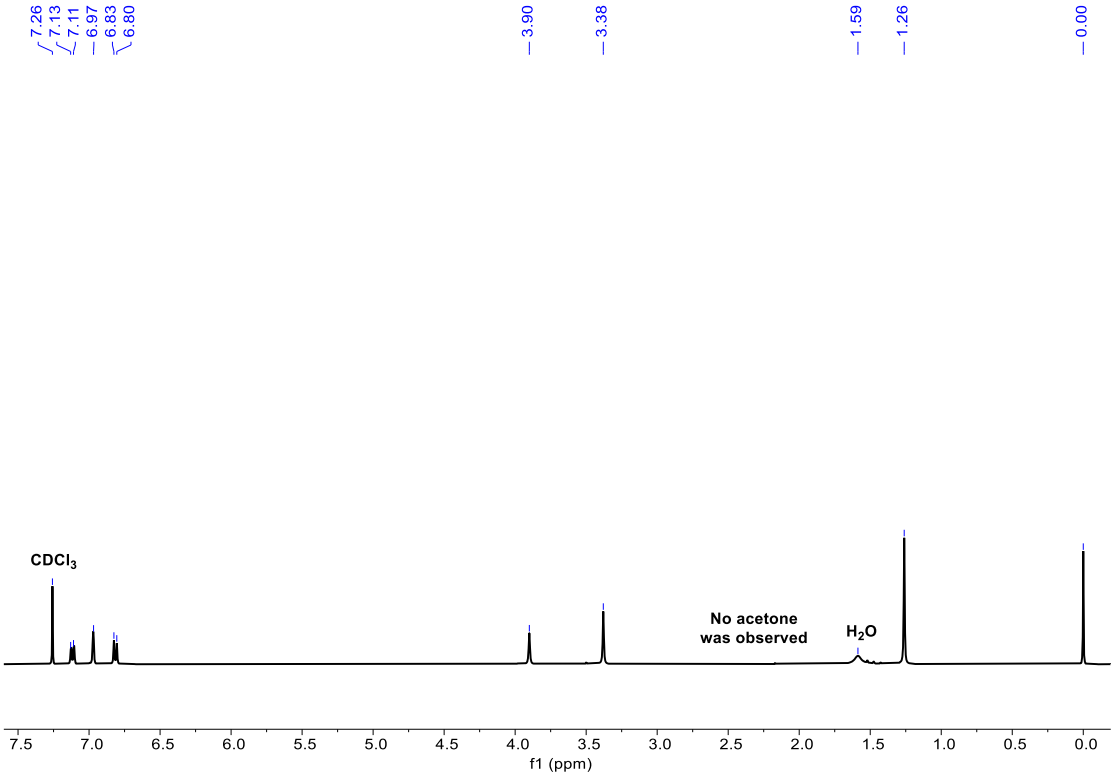


Fig. S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of activated **C[3]A**.

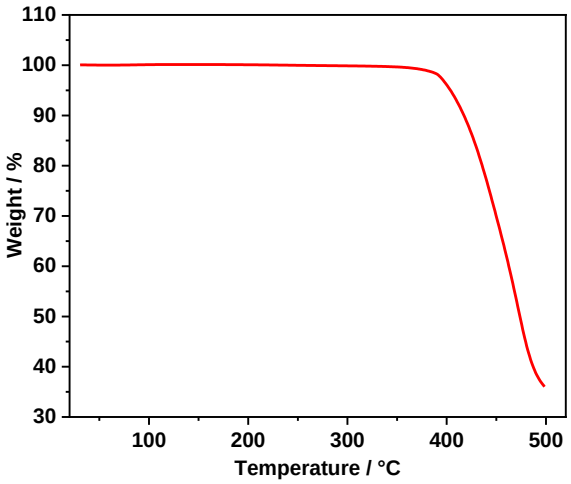


Fig. S5 Thermogravimetric analysis of activated **C[3]A**.

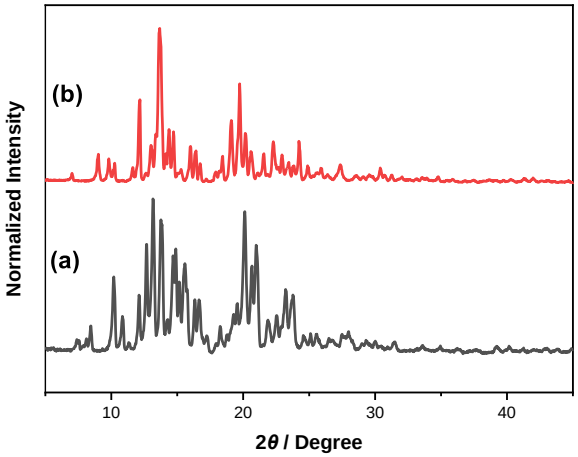


Fig. S6 Power X-ray diffraction pattern of **C[3]A**: (a) recrystallized from acetone and then activated under vacuum at 80 °C; (b) recrystallized from acetone.

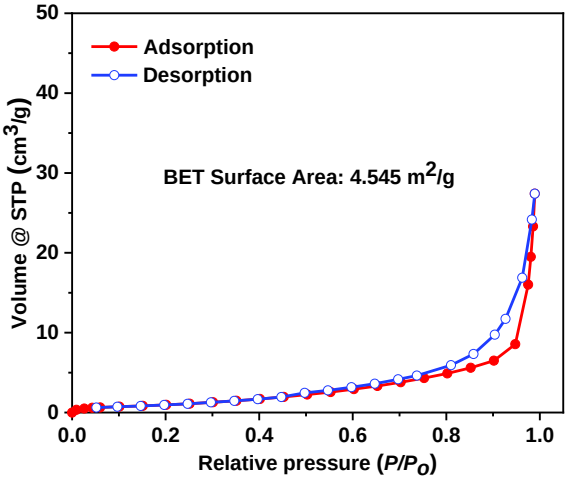


Fig. S7 N_2 adsorption isotherm of activated **C[3]A**. The BET surface area value is 4.545 m^2/g.

4. Solid-vapor adsorption experiments

4.1 Single-component adsorption experiments

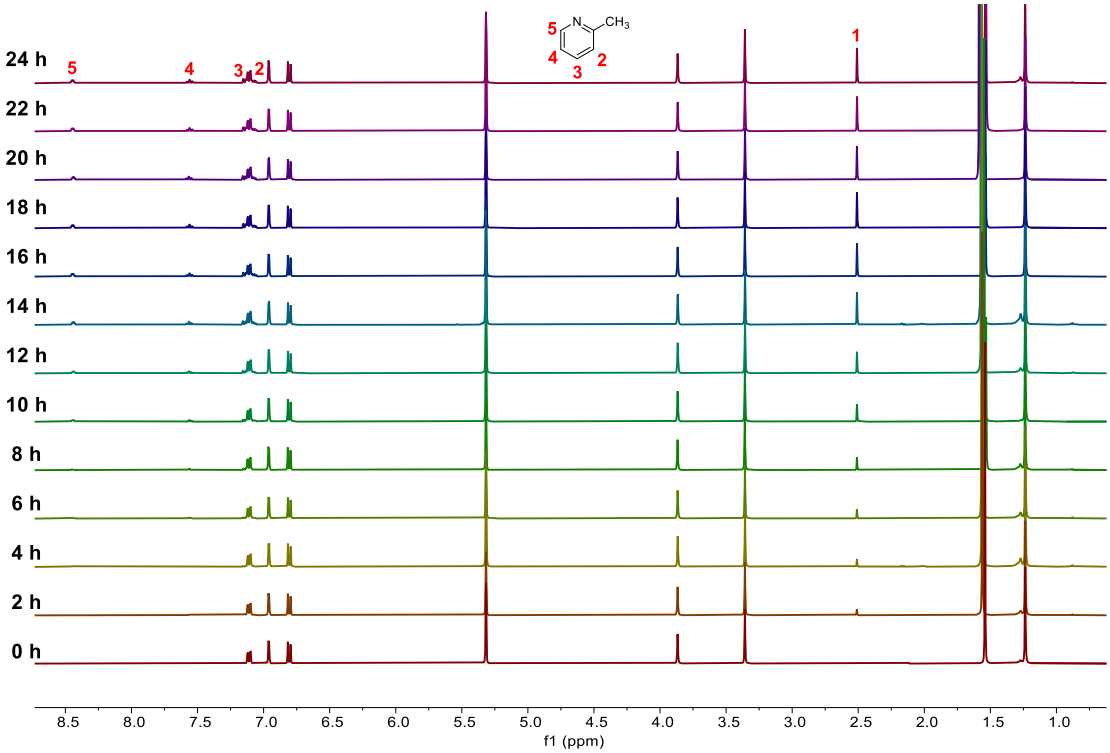


Fig. S8 Time-dependent ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298K) of **C[3]Aα** after adsorption of **2-MP** vapor.

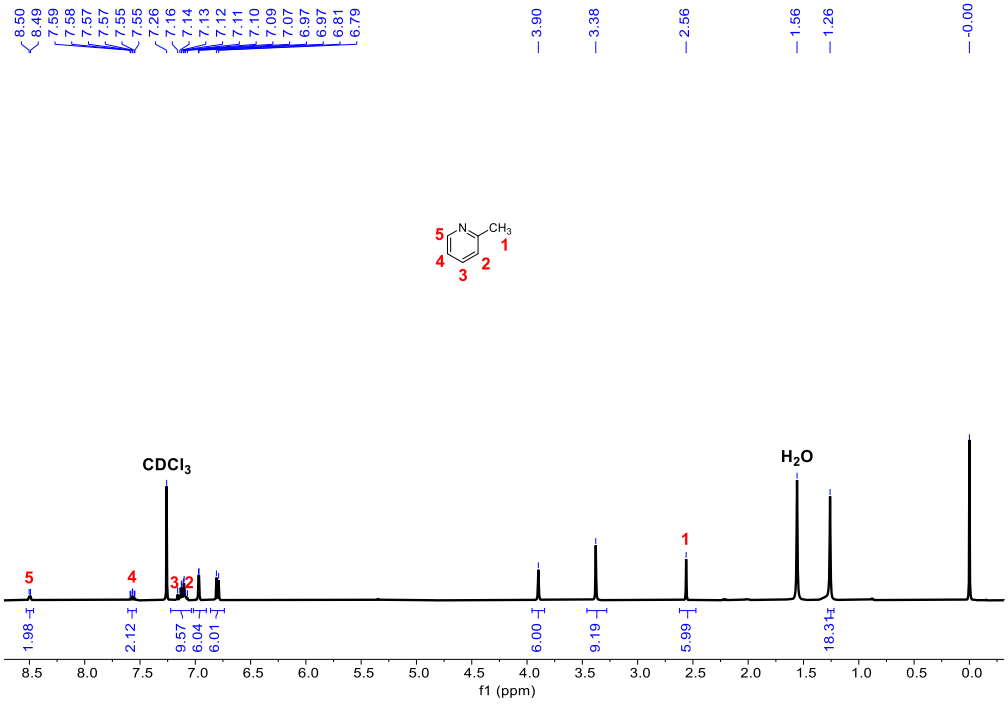


Fig. S9 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **C[3]Aα** after adsorption of **2-MP** vapor for 24 hours.

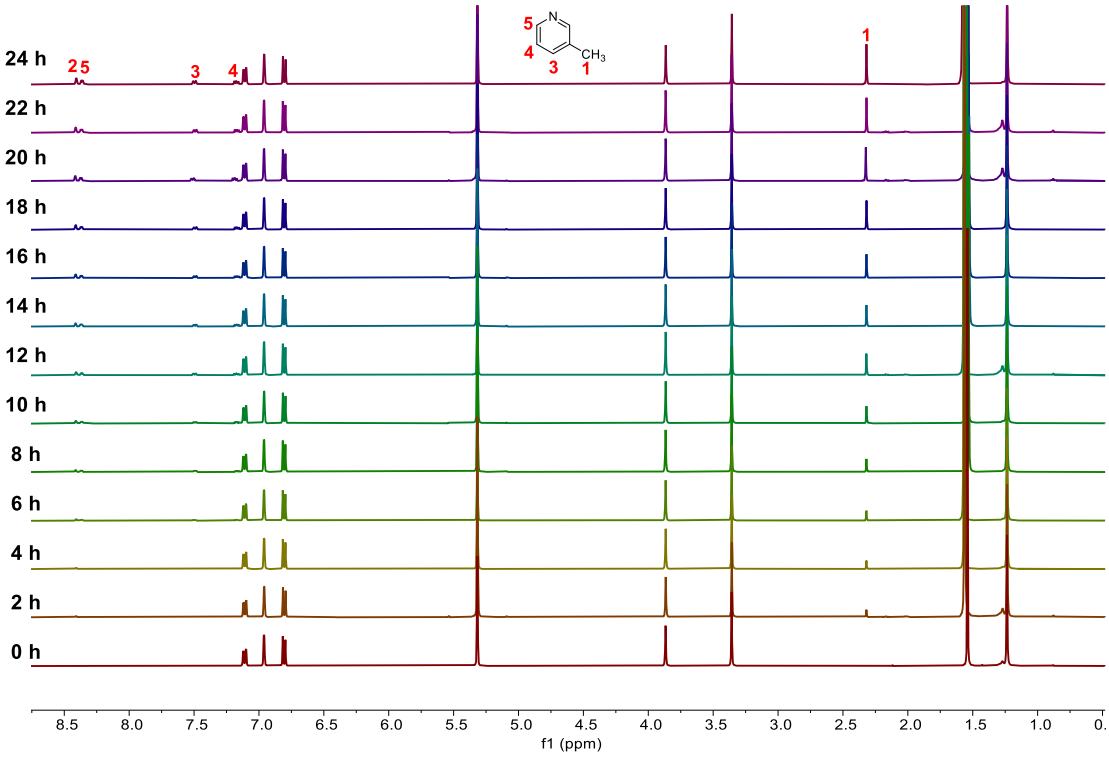


Fig. S10 Time-dependent ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298K) of **C[3]Aα** after adsorption of **3-MP** vapor.

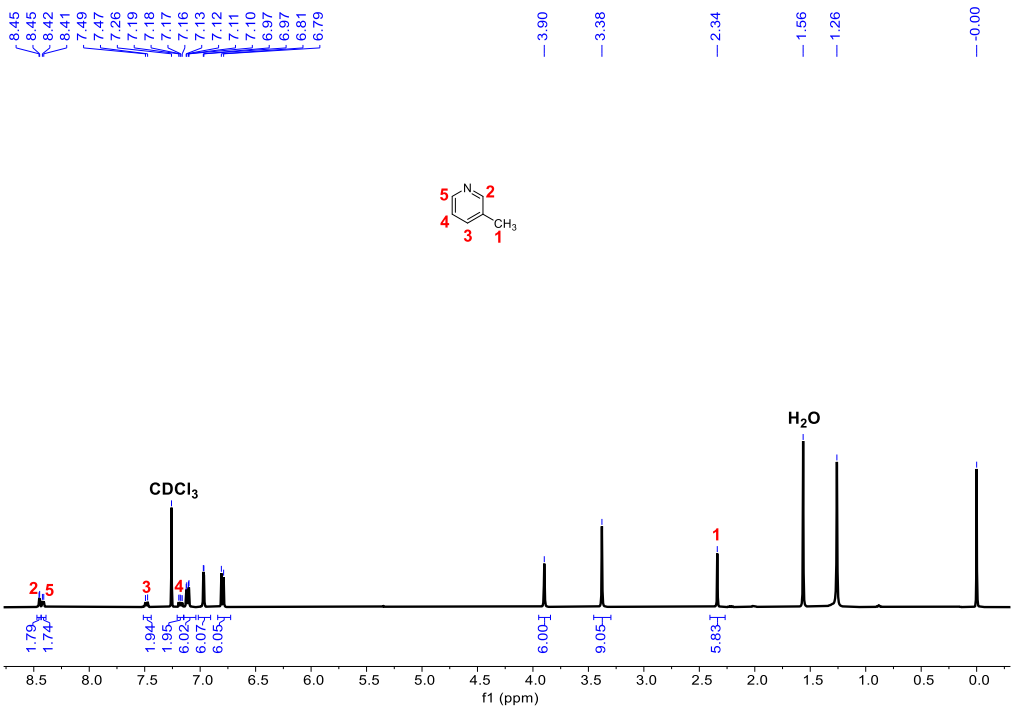


Fig. S11 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **C[3]Aα** after adsorption of **3-MP** vapor for 24 hours.

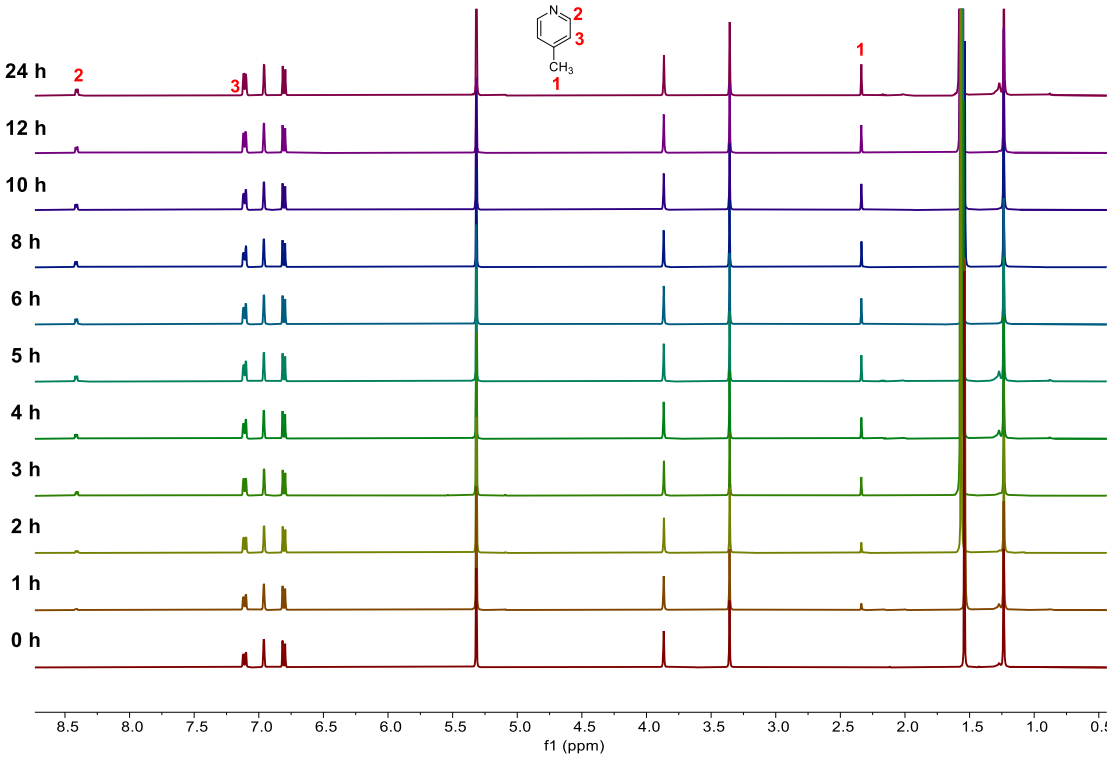


Fig. S12 Time-dependent ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298K) of **C[3]Aα** after adsorption of **4-MP** vapor.

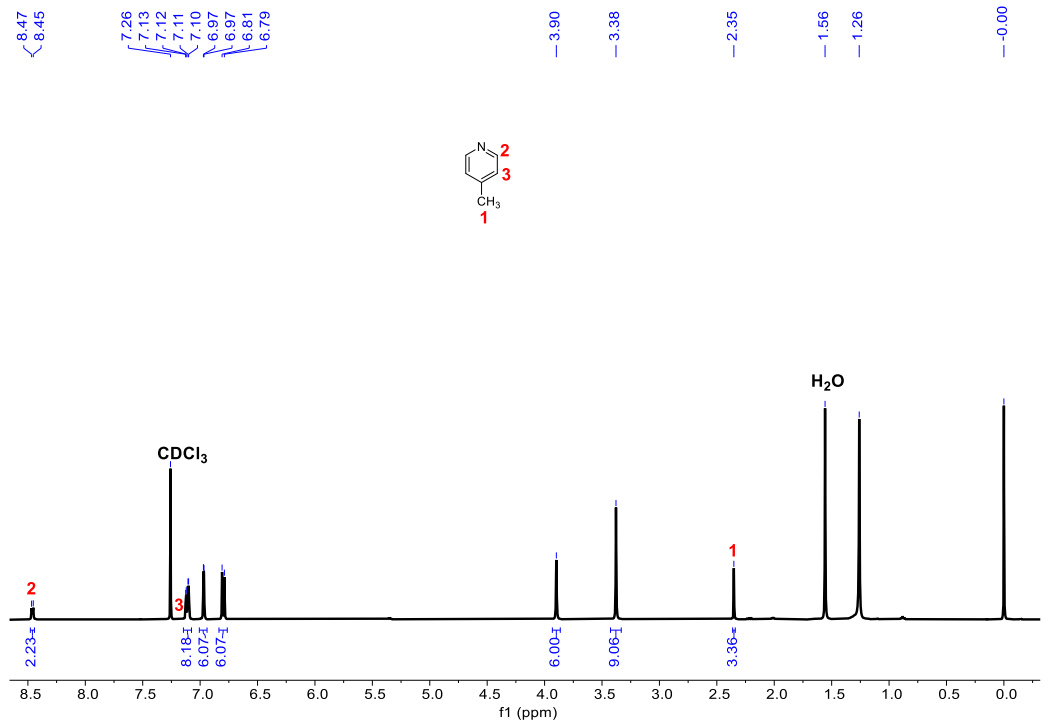


Fig. S13 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **C[3]Aα** after adsorption of **4-MP** vapor for 24 hours.

4.2 Two/Three-component adsorption experiments

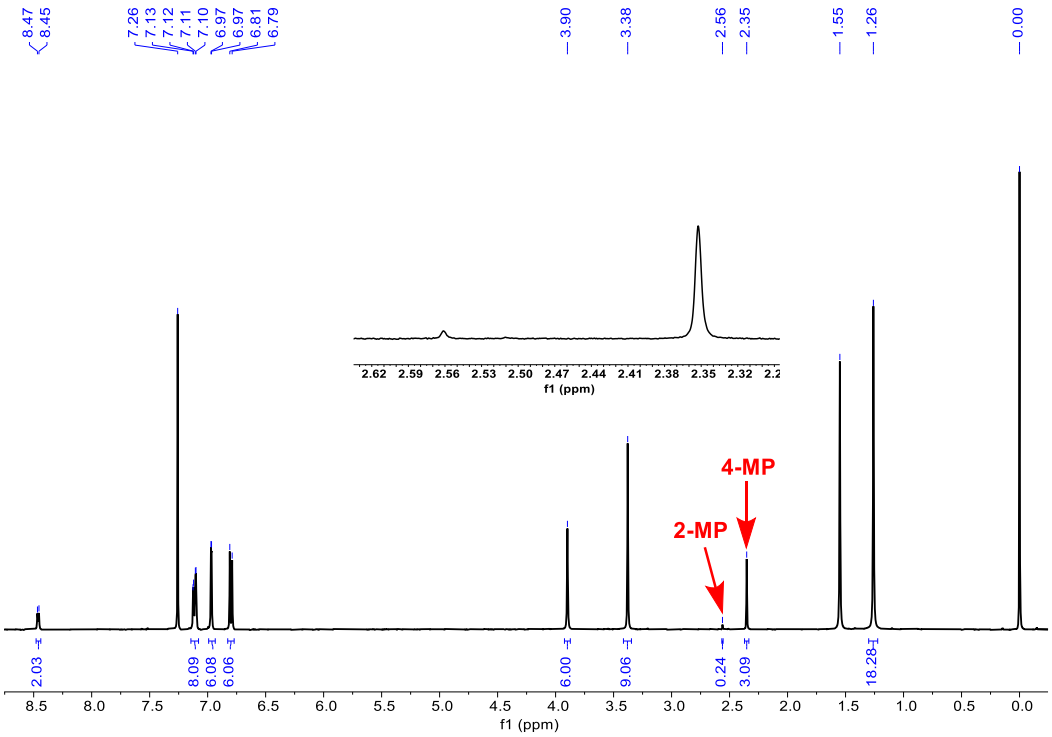


Fig. S14 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **C[3]Aα** after adsorption of **2-MP/4-MP** mixture vapor for 12 hours.

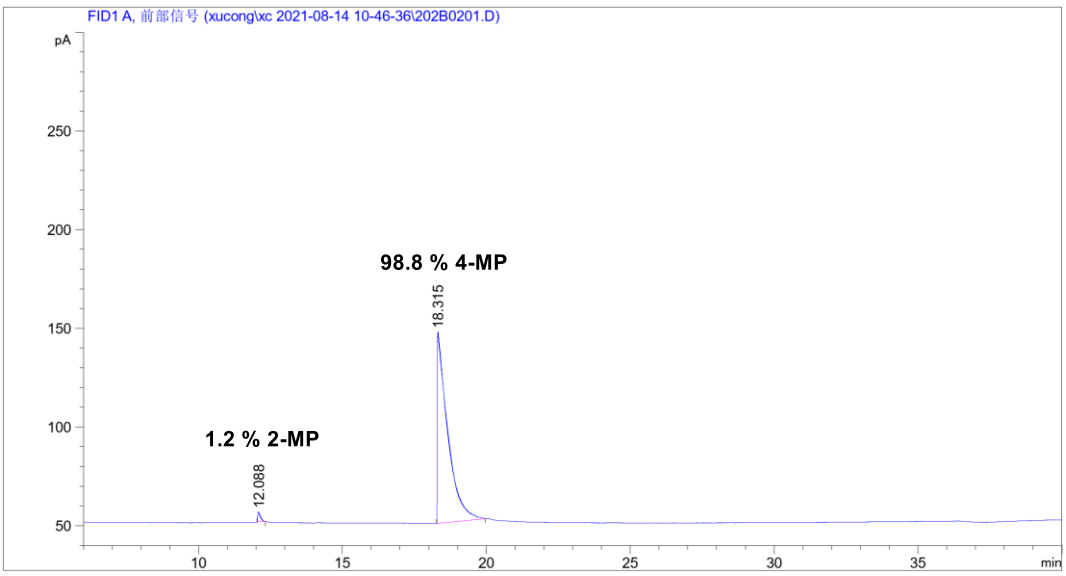


Fig. S15 Relative uptake of the **2-MP/4-MP** mixture vapor adsorbed in **C[3]A** determined by gas chromatography.

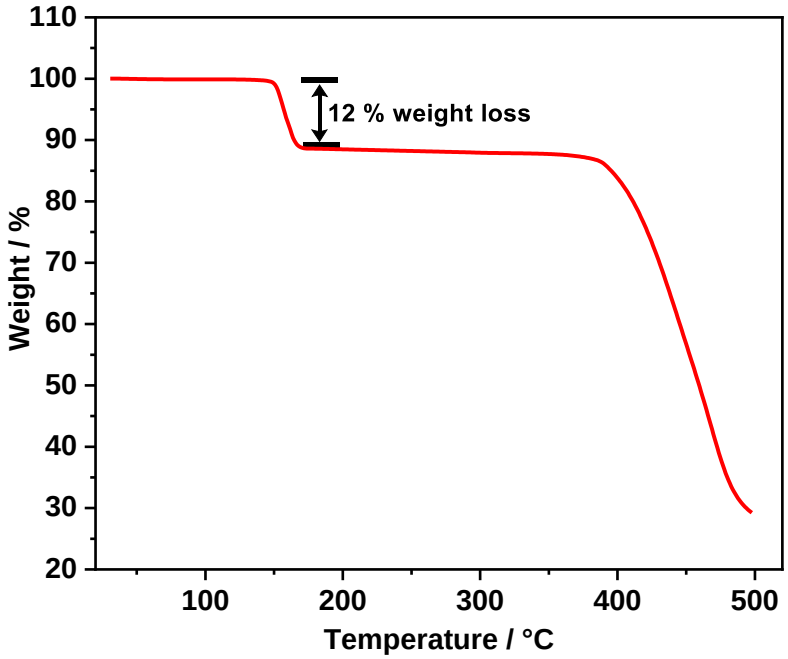


Fig. S16. Thermogravimetric analysis of **C[3]Aα** after adsorption of **2-MP**/**4-MP** mixture vapor for 12 hours.

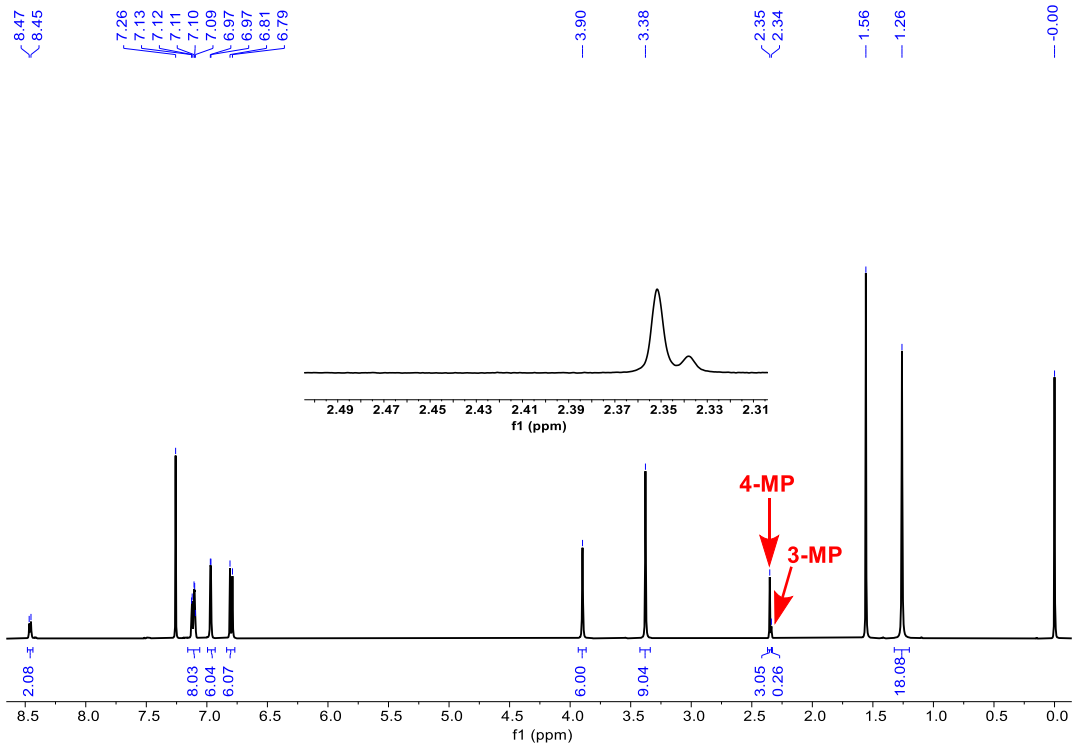


Fig. S17 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **C[3]Aα** after adsorption of **3-MP**/**4-MP** mixture vapor for 12 hours.

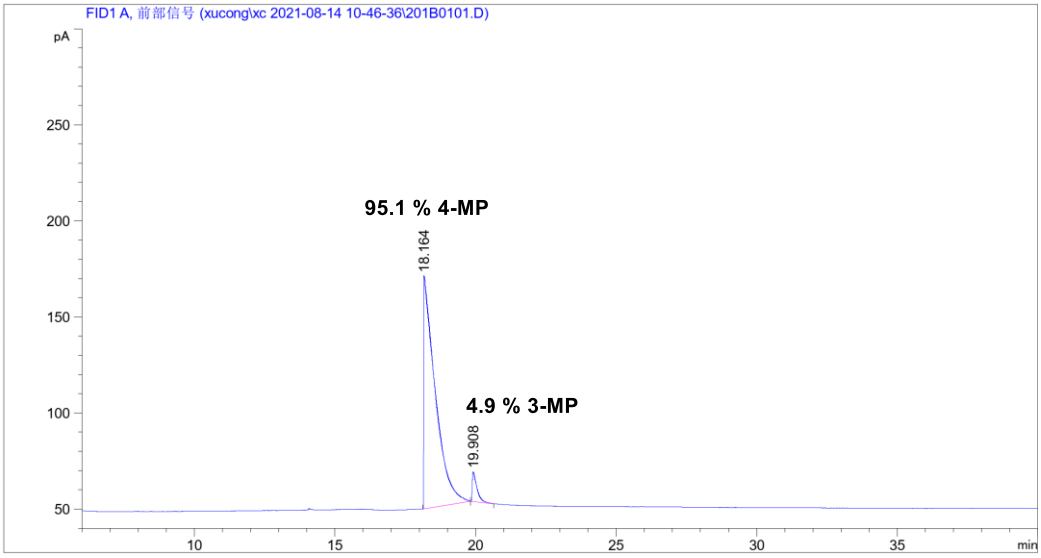


Fig. S18 Relative uptake of the **3-MP**/**4-MP** mixture vapor adsorbed in **C[3]A** determined by gas chromatography.

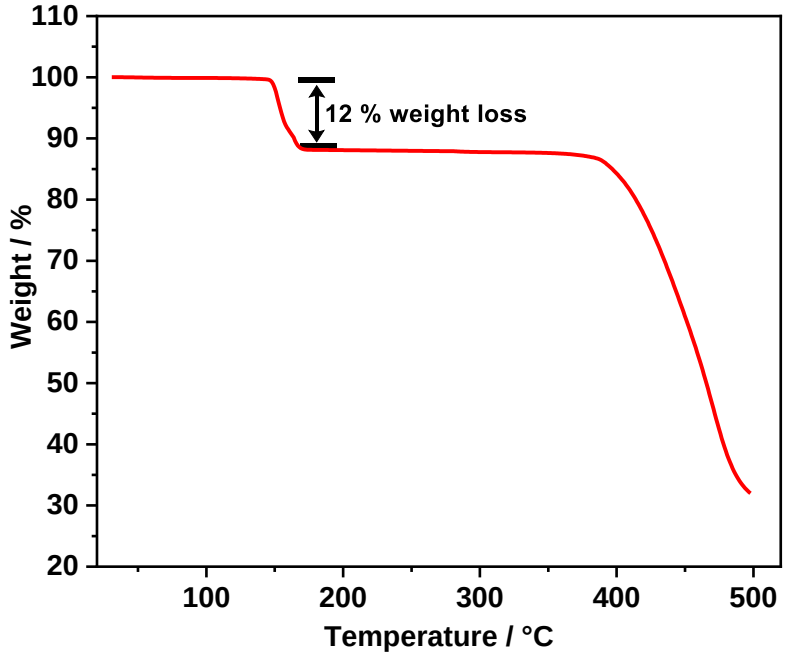


Fig. S19 Thermogravimetric analysis of **C[3]Aα** after adsorption of **3-MP**/**4-MP** mixture vapor for 12 hours.

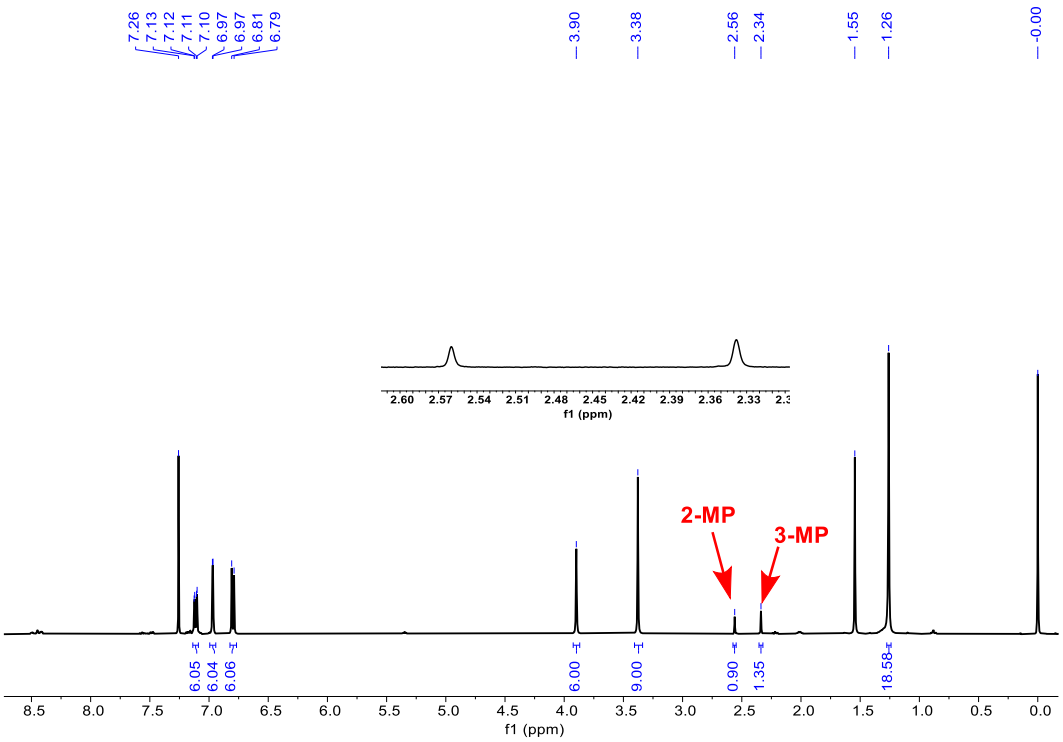


Fig. S20 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **C[3]Aα** after adsorption of **2-MP/3-MP** mixture vapor for 12 hours.

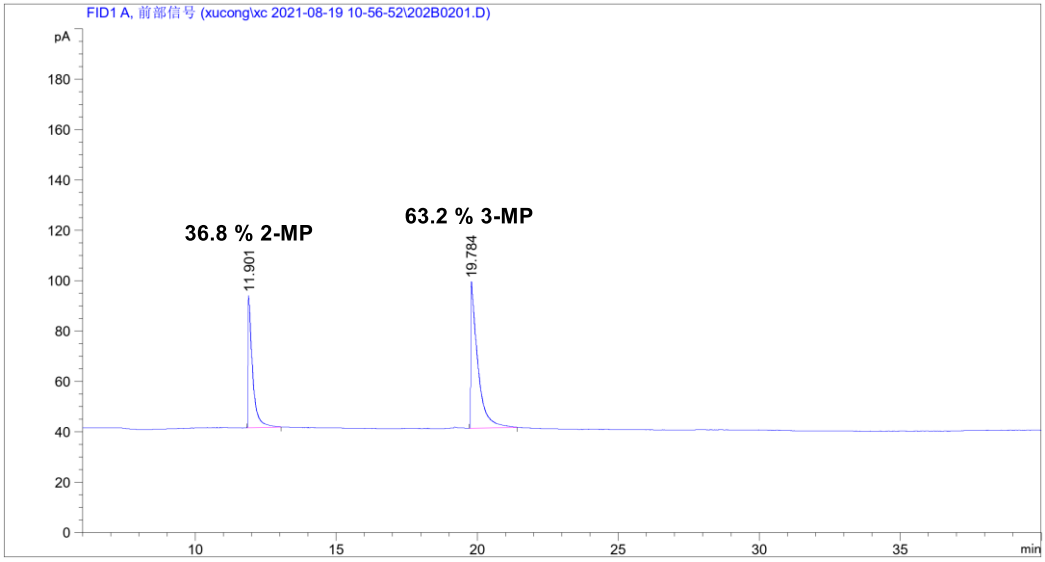


Fig. S21 Relative up of the **2-MP/3-MP** mixture vapor adsorbed in **C[3]A** determined by gas chromatography.

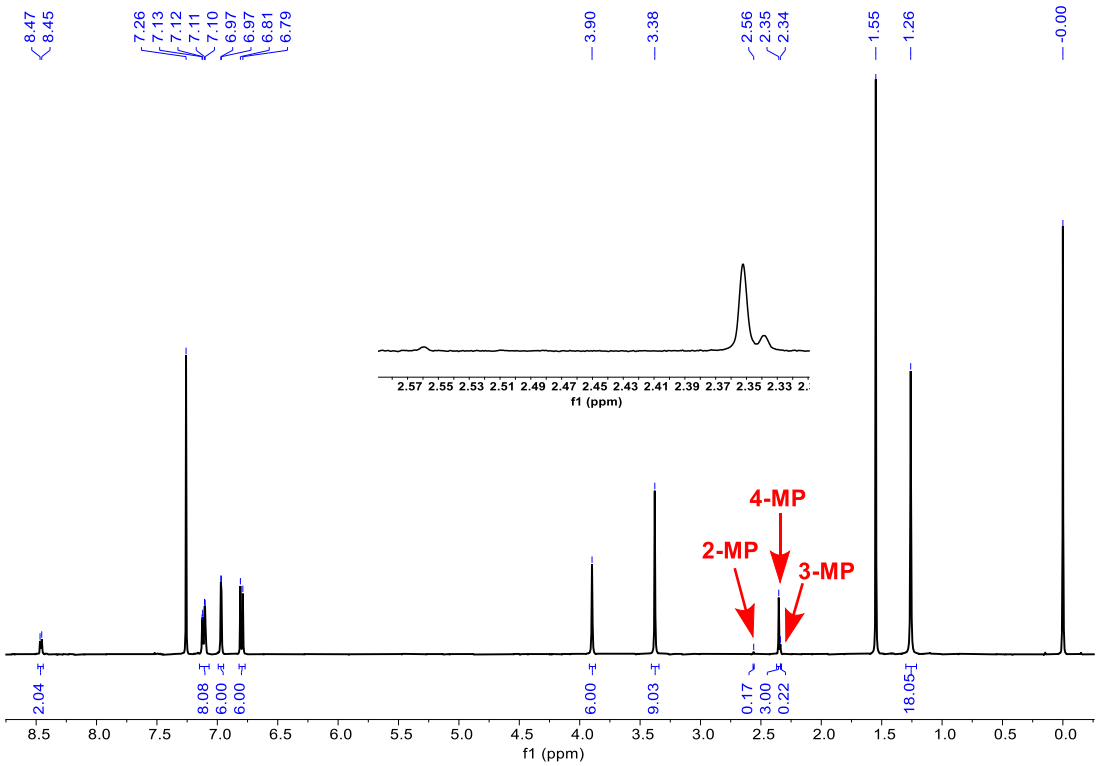


Fig. S22 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **C[3]Aα** after adsorption of **2-MP/3-MP/4-MP** mixture vapor for 12 hours.

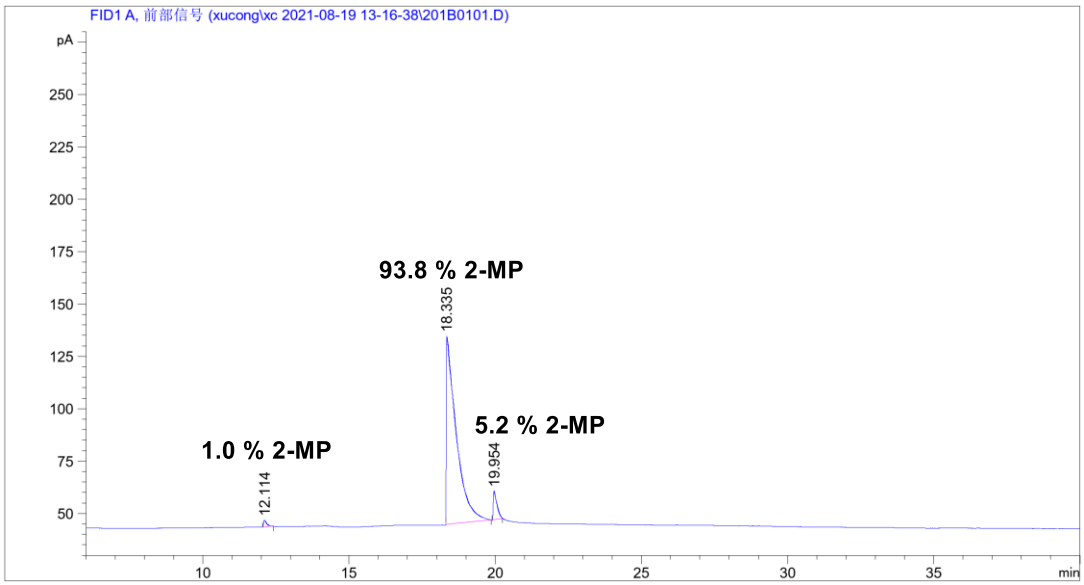


Fig. S23 Relative up of the **2-MP/3-MP/4-MP** mixture vapor adsorbed in **C[3]A** determined by gas chromatography.

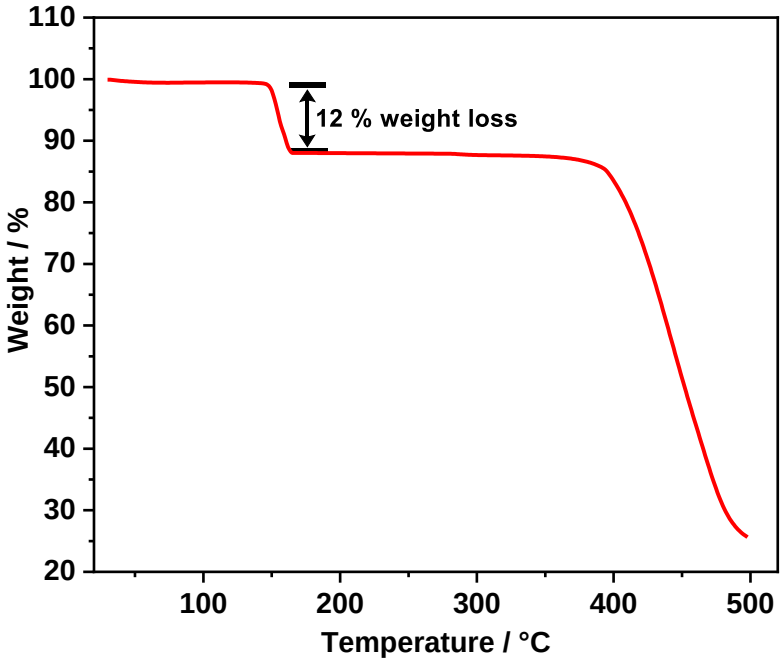


Fig. S24 Thermogravimetric analysis of **C[3]Aα** after adsorption of **2-MP/3-MP/4-MP** mixture vapor for 12 hours.

4.3 Cyclic adsorption experiments

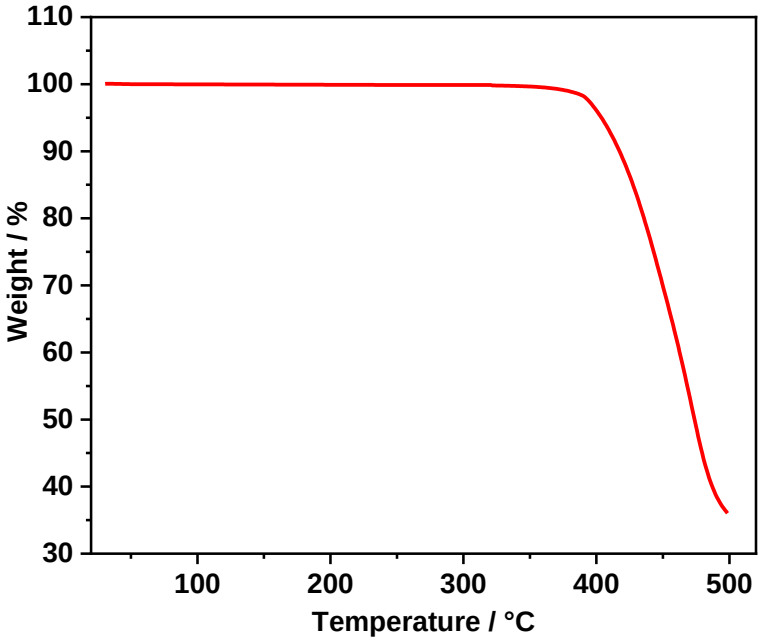


Fig. S25 Thermogravimetric analysis of desolvated **4-MP**-loaded **C[3]A** crystals upon removel of **4-MP**.

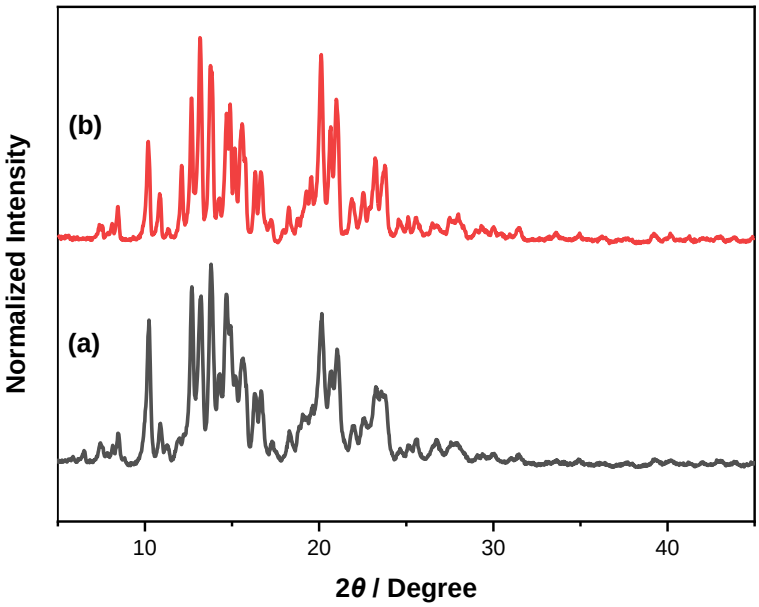


Fig. S26 Power X-ray diffraction patterns of **C[3]A**: (a) desolvated **4-MP**-loaded **C[3]A** crystals; (b) original **C[3]Aα**.

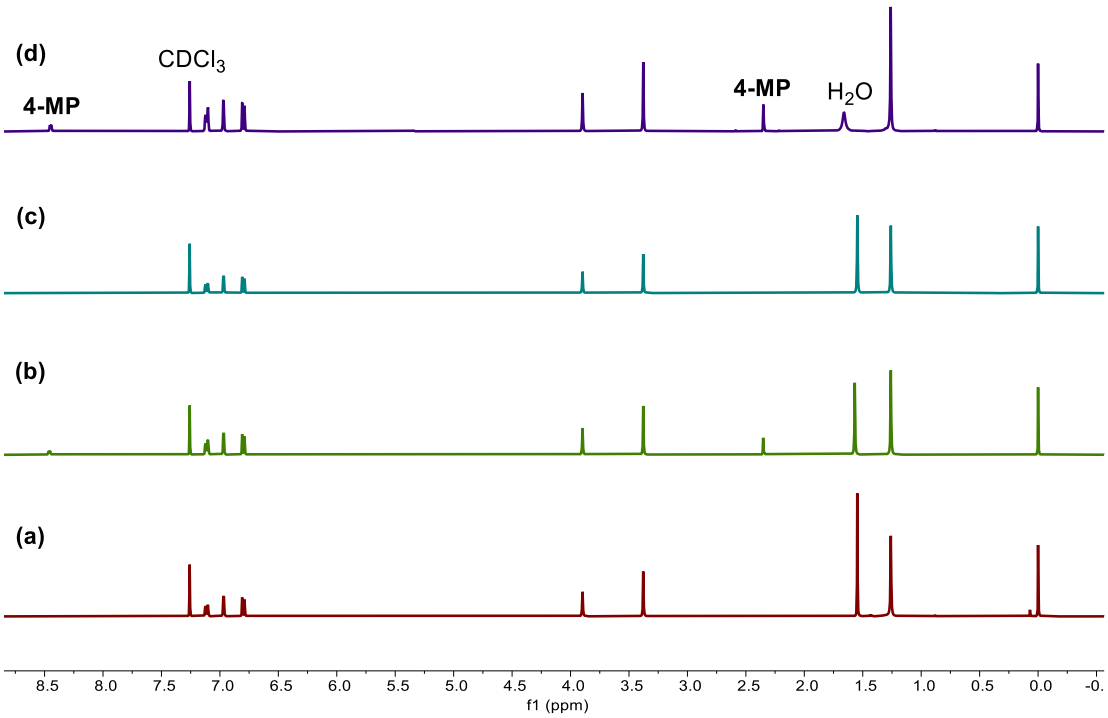


Fig. S27 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of (a) original **C[3]Aα**; (b) **C[3]Aα** after adsorption of **2-MP/3-MP/4-MP** mixture vapor; (c) **4-MP**-loaded **C[3]A** crystals after removal of **4-MP**; (d) desolvated **4-MP**-loaded **C[3]A** crystals after adsorption of **2-MP/3-MP/4-MP** mixture vapor.