Supporting Information

Selective Separation of 2,5-Dimethylfuran and 2,5-Dimethyltetrahydrofuran using Nonporous Adaptive Crystals of a Hybrid[3]arene

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1. Materials

All starting materials including 2,5-dimethylfuran (**DMeF**) and 2,5-dimethyltetrahydrofuran (**DMeTHF**) were purchased commercially and used as received. Hybrid[3]arene (**HB3**) was synthesized as described previously.[S1] Activated crystalline **HB3** was denoted as **HB3***α*. **HB3***α* was prepared according to the previous report.[S2] All the mixture in this work were *v*:*v* = 1:1 unless specifically noted.

Table S1 Physical properties of **DMeF** and **DMeTHF**.[S3]

Substance	Melting point (℃)	Boiling point (℃)	Saturated vapor pressure at 298 K (kPa)
DMeF	–62.8	96.0	57.1 ± 0.2 mmHg
DMeTHF	–62.8	91.0	62.1 ± 0.1 mmHg

2. Methods

2.1. Powder X-Ray Diffraction (PXRD)

The 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 5–35° in 5°/min steps over 8 min.

2.2. Thermogravimetric Analysis (TGA)

TGA analysis 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.

2.3. Single Crystal Growth

Single crystals of **DMeF@HB3** were grown by placing 5.00 mg of dry **HB3** powder in a small vial, adding 1 mL of **DMeF**, heating until all the powder was dissolved, and allowing to evaporate at room temperature about one week.

2.4. Single Crystal X-ray Diffraction (SCXRD) Analyses

Single crystal X-ray diffraction data were collected on a Bruker D8 VENTURE CMOS X-ray diffractometer with a graphite monochromated Mo–Kα radiation (λ = 0.71073 Å).

2.5. Solution ^{1}H NMR Spectroscopy

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker Avance III DMX 400 spectrometer, a Bruker Avance III DMX 500 spectrometer, and an Agilent DD2-600 spectrometer.

2.6. Gas Chromatography (GC)

Gas chromatography analysis: GC measurements were carried out using an Agilent 7890B instrument configured with a 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 120 °C for 30 min followed by sampling 1.00 mL of the headspace. The following 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; helium (carrier gas) flow-rate was 3.0 mL min^{-1}. The samples were injected in the split mode (30:1).

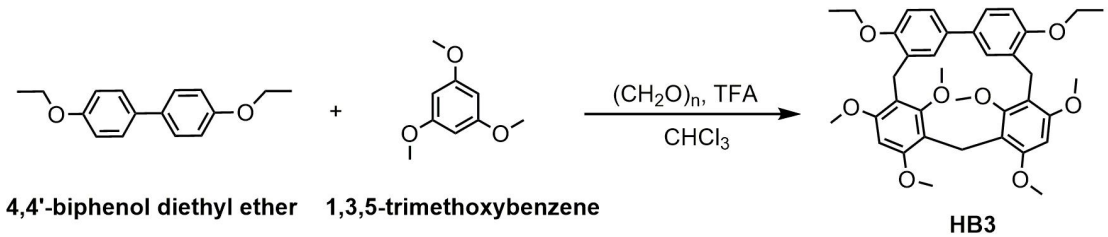
2.7. Gas sorption measurements

N_2 adsorption and desorption isotherms for the activated materials were measured at 77 K using a JW-BK200C 2 instrument.

2.8. Theoretical calculations

The geometry optimization and density functional theory (DFT) chemical description for the molecular structures of all **DMeF** and **DMeTHF** compounds were performed using Gaussian09 program[S4] package with M062X exchange-correlation functional and 6-311G** basis set[S5–S6].

3. Characterization of Activated Hybrid[3]arene



Scheme S1. Synthetic route to hybrid[3]arene (**HB3**)

Synthesis of **HB3**: To the solution of 4,4'-biphenol diethyl ether (2.42 g, 10.0 mmol) and 1,3,5-trimethoxybenzene (3.36 g, 20.0 mmol) in $CHCl_3$ (200 mL), paraformaldehyde (0.900 g, 30.0 mmol) and trifluoroacetic acid (TFA, 10 mL) were added. The mixture was refluxed for 30 min, and the progress was monitored by thin-layer chromatography (TLC). The mixture was cooled to room temperature, and an excess of saturated aqueous Na_2CO_3 was added to neutralize TFA. The organic phase was separated and the crude product was purified by column chromatography (petroleum ether/ CH_2Cl_2, *v*/*v* 10:1 to 3:1) to get **HB3** as a white solid (1.67 g, 25%).

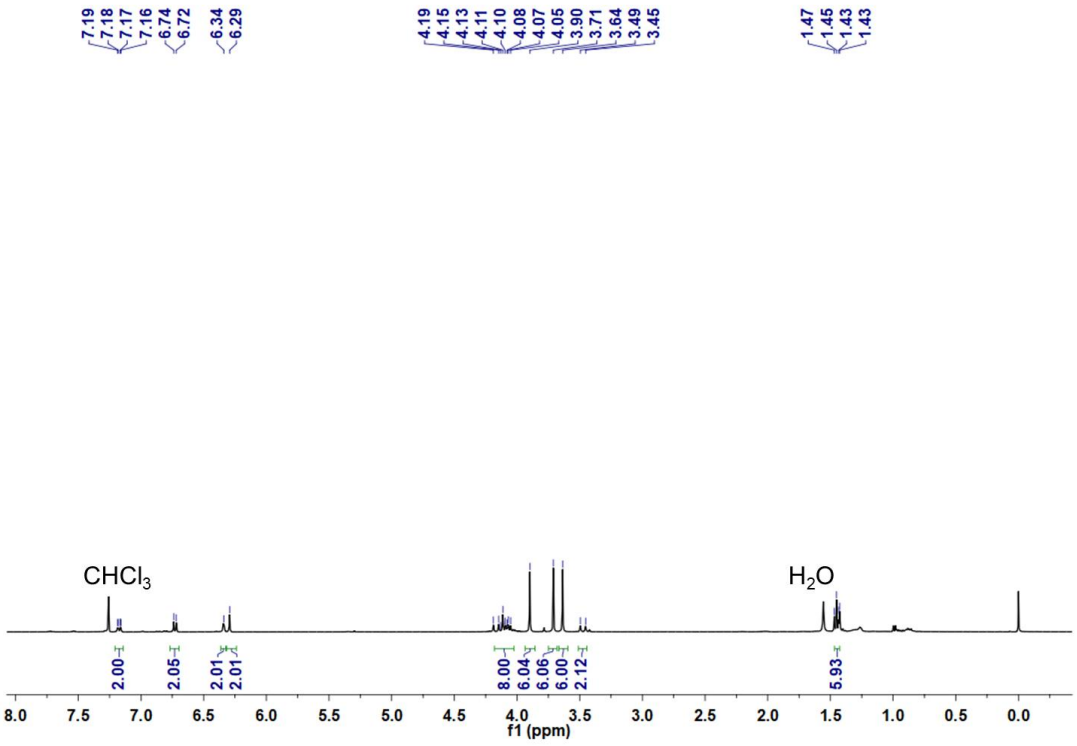


Fig. S1. ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of **HB3**.

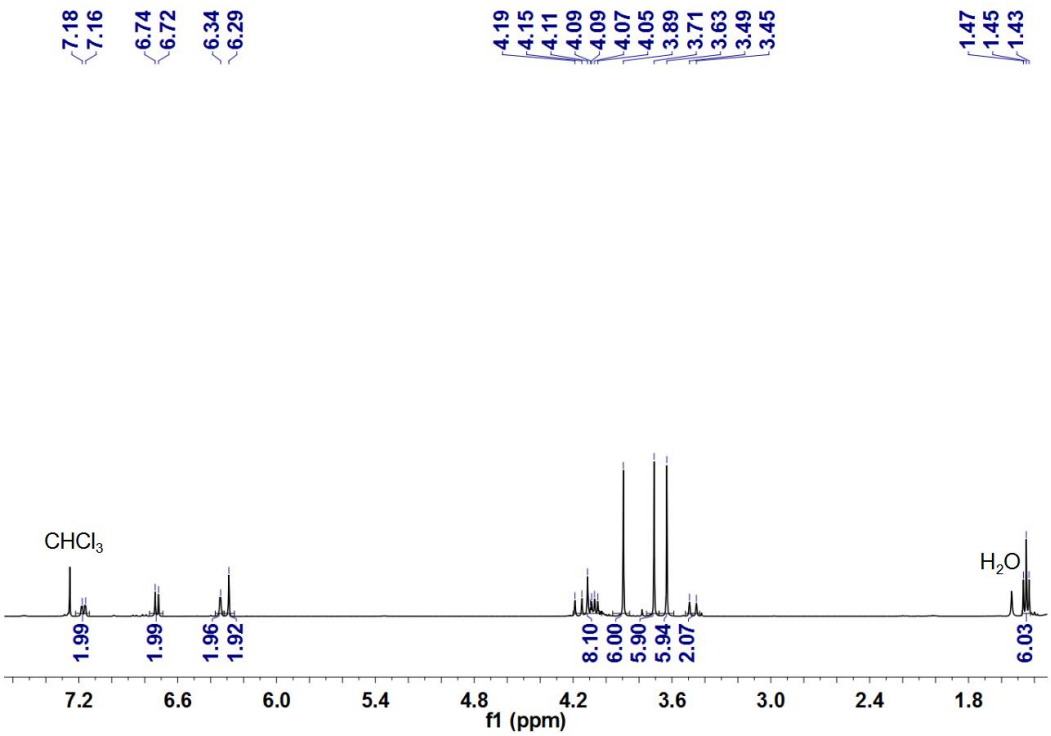


Fig. S2. ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of **HB3***α*.

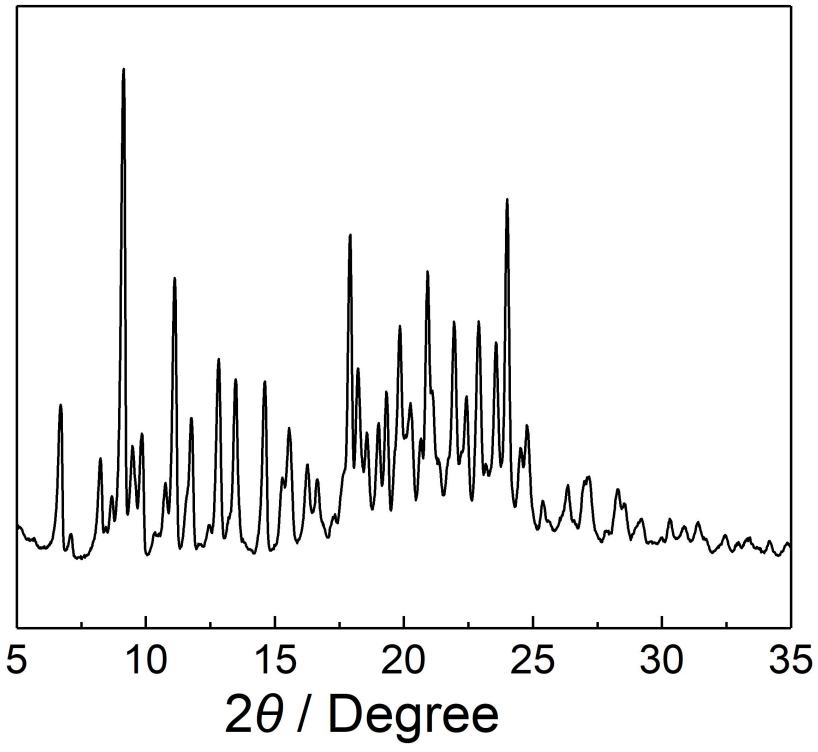


Fig. S3. PXRD pattern of **HB3***α*.

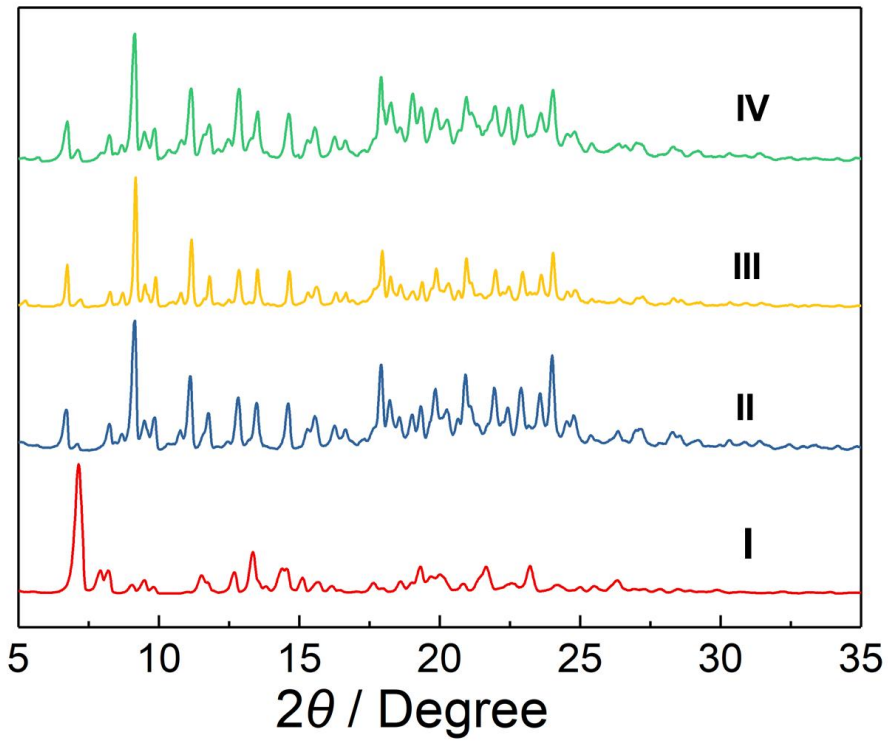


Fig. S4. PXRD patterns of (I) as-synthesized **HB3**; (II) **HB3** under vacuum; (III) high temperature; (IV) humid environment conditions.

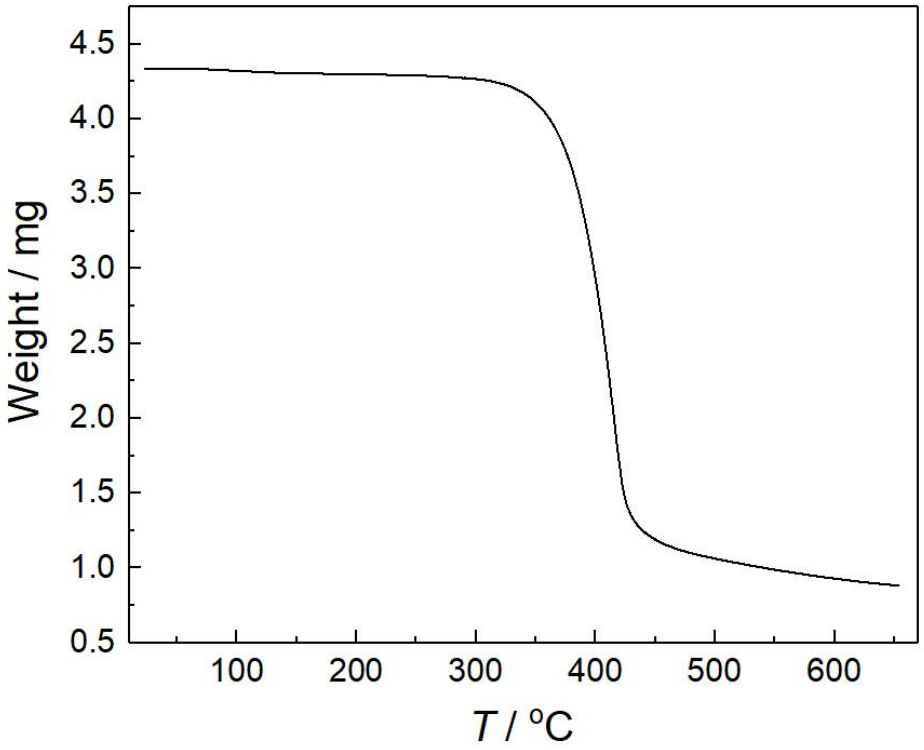


Fig. S5. TGA curve of desolvated **HB3***α*.

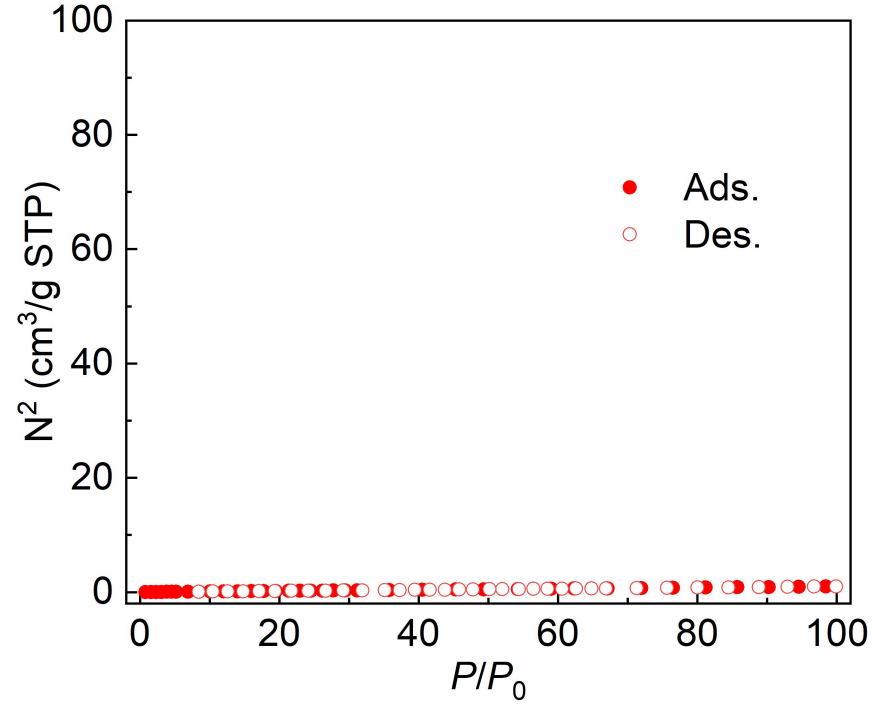


Fig. S6. Experimental N_2 adsorption isotherms at 77 K measuring the porosity of activated **HB3***α*. The apparent Brunauer-Emmett-Teller (BET) surface area is calculated to be 2 m^2/g, indicating **HB3***α* is nonporous.

4. Solid–Vapor Adsorption Experiments of Hybrid[3]arene

4.1. Single-Component DMeF and DMeTHF Adsorption Experiments

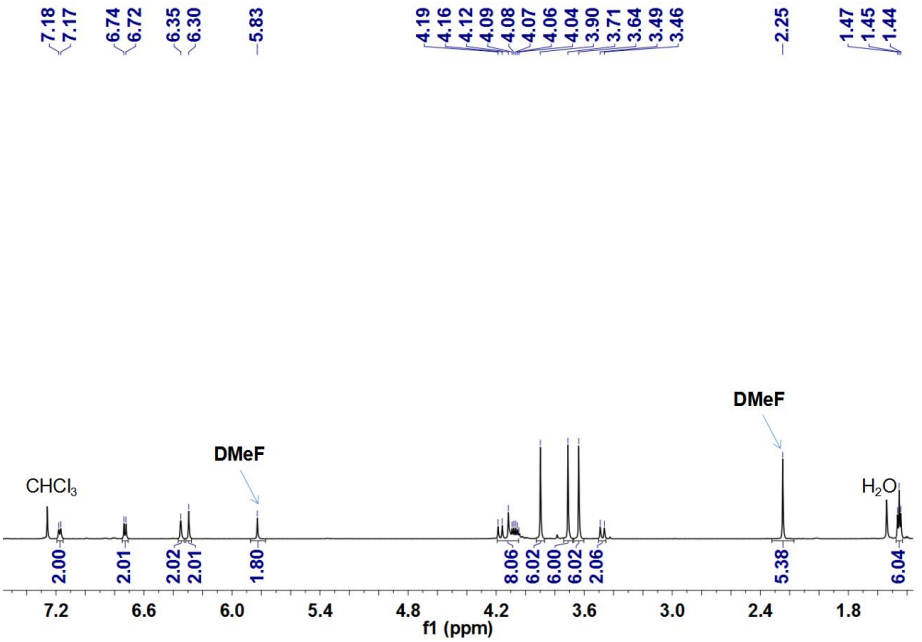


Fig. S7. ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of **HB3***α* after adsorption of **DMeF** vapor.

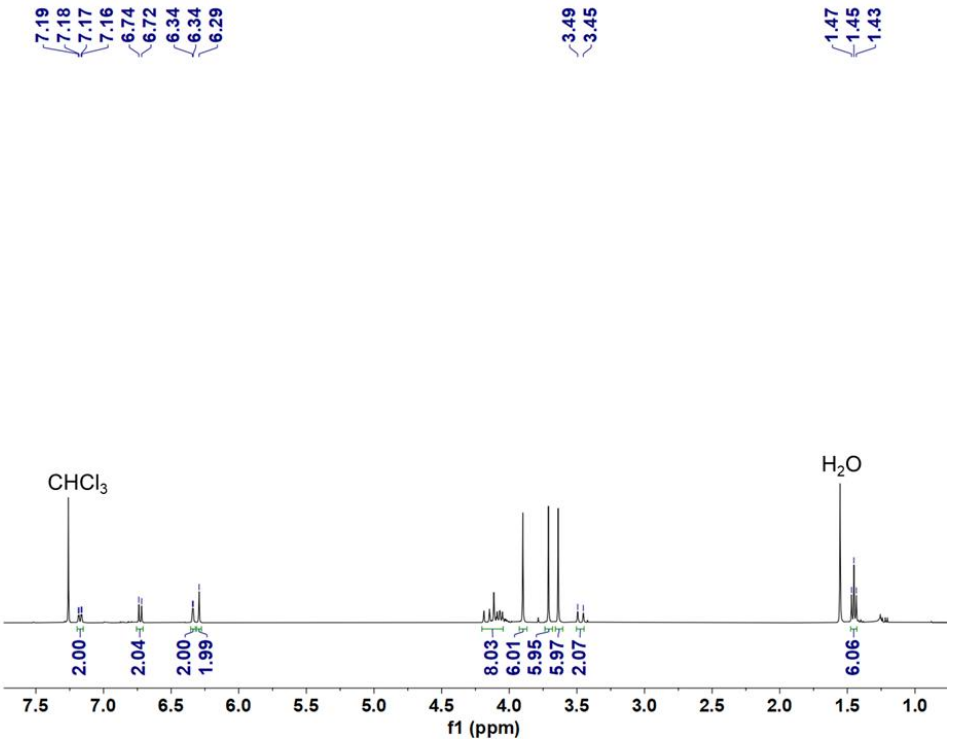


Fig. S8. ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of **HB3***α* after adsorption of **DMeTHF** vapor.

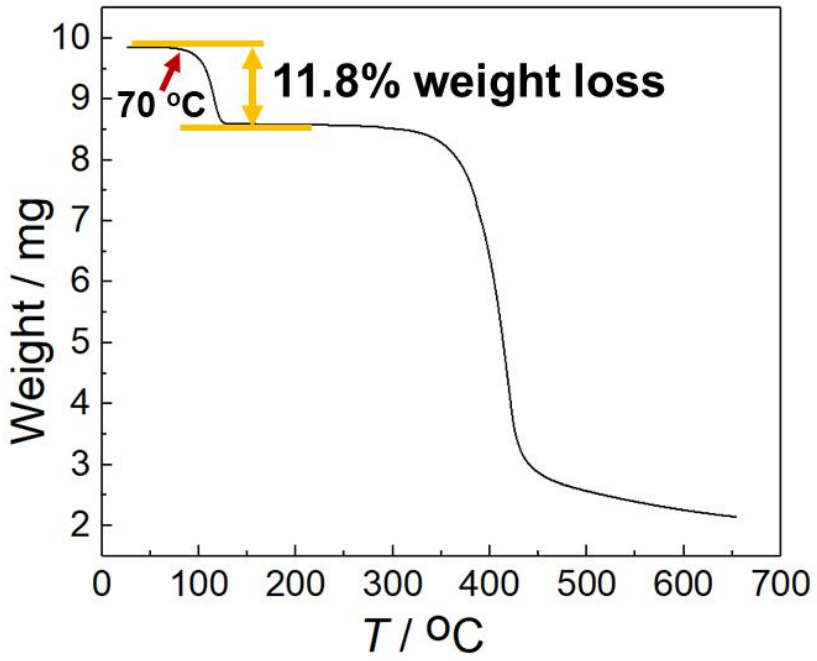


Fig. S9. TGA curve of desolvated **HB3***α* after adsorption of **DMeF** vapor. The weight loss below 150 ℃ can be calculated to one equivalent of **DMeF** molecule *per* **HB3** molecule.

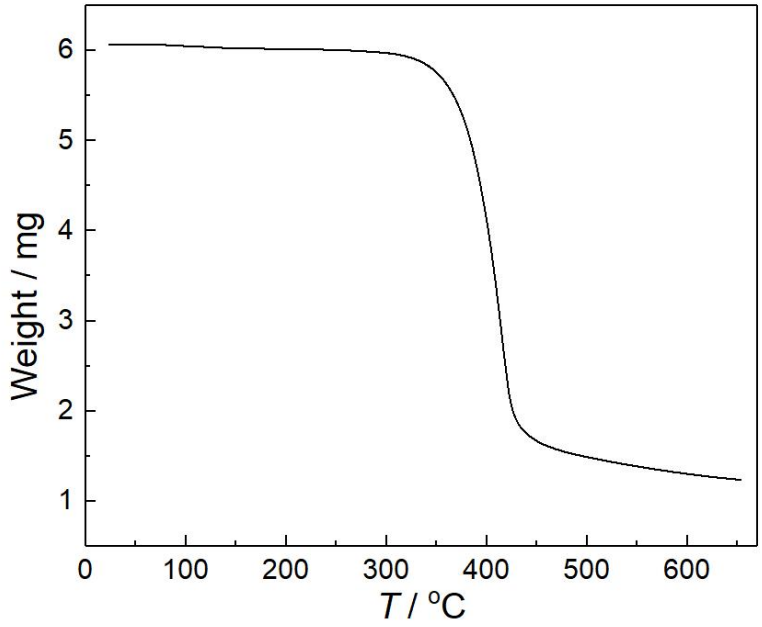


Fig. S10. TGA curve of desolvated **HB3***α* after adsorption of **DMeTHF** vapor. TGA results revealed no weight loss, indicating no uptake of **DMeTHF** vapor.

4.2. Structural Analyses of Single-Component Vapor Adsorption Experiments

Table S2. Experimental single crystal X-ray diffraction data of **DMeF@HB3** structure.

Formula	**DMeF@HB3**
Empirical formula	$C_{43}H_{50}O_9$
Formula weight	710.83
Temperature/K	169.99
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	10.8040(3)
b/Å	13.0735(3)
c/Å	15.6468(4)
α/°	109.2350(10)
β/°	97.967(2)
γ/°	107.3160(10)
Volume/Å^3	1922.21(9)
Z	2
ρ_{calc}(g/cm^3)	1.228
μ/mm^{-1}	0.443
F(000)	760
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	6.754 to 109.886
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 15$, $-19 \le l \le 19$
Reflections collected	19307
Independent reflections	7275 [R_{int} = 0.0894, R_{sigma} = 0.0986]
Data/restraints/parameters	7275/210/546
Goodness-of-fit on F^2	1.018
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0807, wR_2 = 0.2057
Final R indexes [all data]	R_1 = 0.1151, wR_2 = 2377
Largest difference peak/hole/e Å^{-3}	0.35/–0.41
CCDC-number	1975518

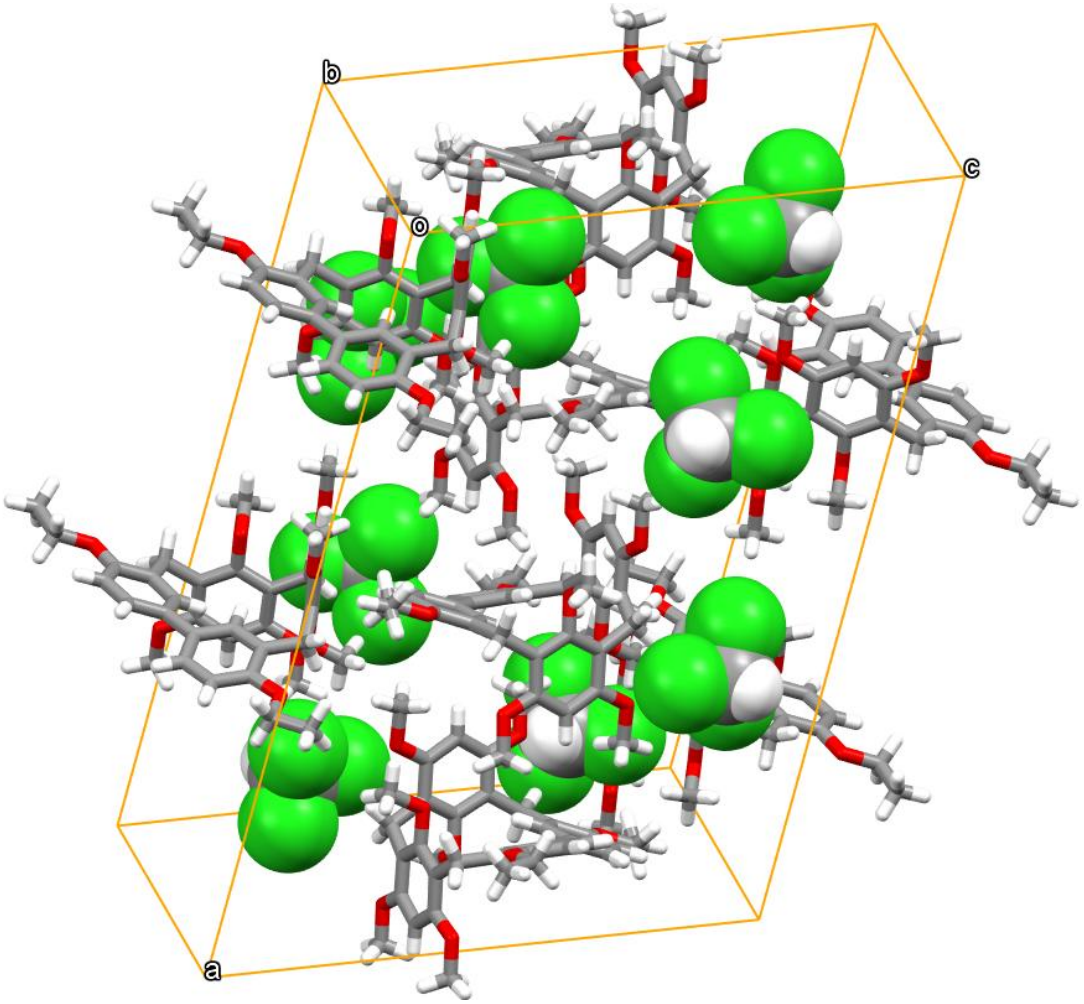


Fig. S11. Capped-stick and spacefill representation of the single crystal structure of **$CHCl_3$@HB3** in a unit cell. The elementary cell is marked with an orange cuboid (a = 28.16(6) Å, b = 14.15(3) Å, c = 19.61(4) Å, α = 90°, β = 106.28(10)°, γ = 90°, space group: $C2/C$). Carbon atoms are grey, oxygen atoms are red, chlorine atoms are green, and hydrogen atoms are white.

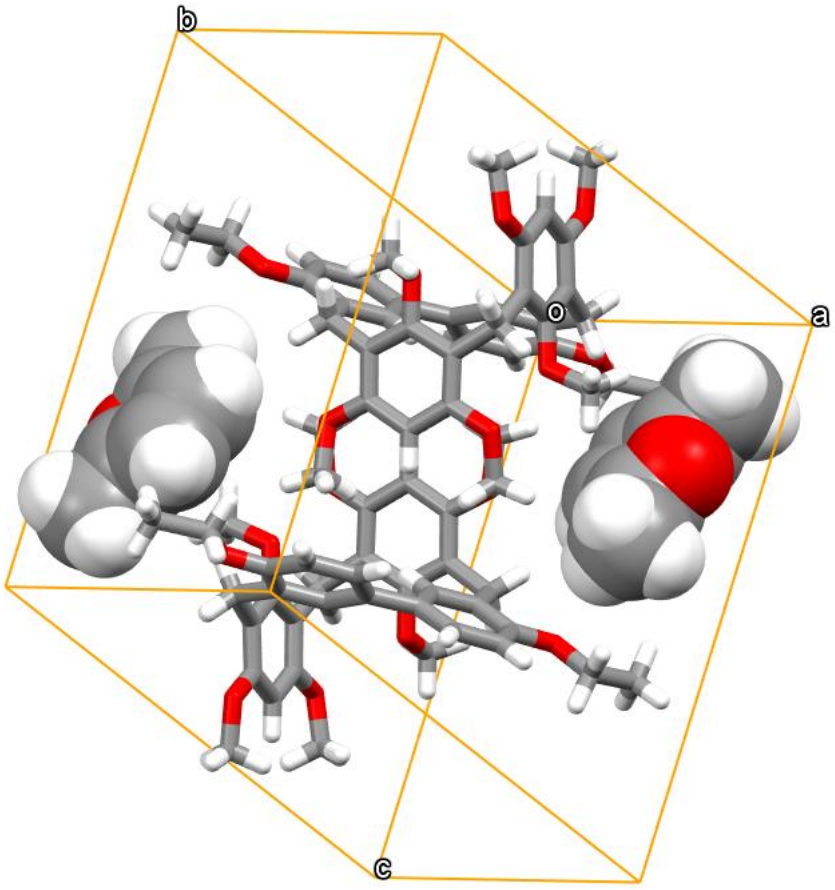


Fig. S12. Capped-stick and spacefill representation of the single crystal structure of **DMeF@HB3** in a unit cell. Carbon atoms are grey, oxygen atoms are red, and hydrogen atoms are white. The elementary cell is marked with an orange cuboid (a = 10.80(3) Å, b = 13.07(3) Å, c = 15.65(4) Å, α = 109.24(10)°, β = 97.98(2)°, γ = 107.32(10)°, space group: $P\bar{1}$). Compared with the single crystal structure of **$CHCl_3$@HB3**, the unit cell parameters have obvious difference, this also indicates the adaptive nature of **HB3** crystals.

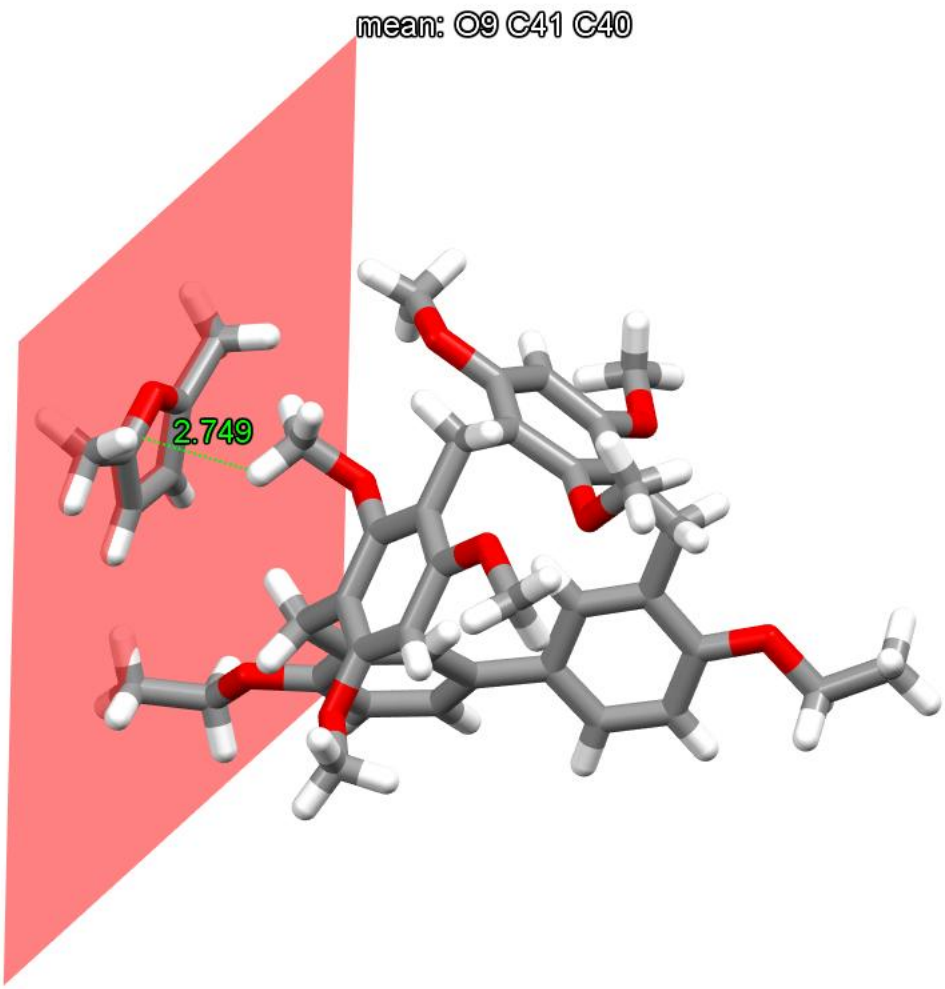


Fig. S13. Capped-stick representation of the single crystal structure of **DMeF@HB3**. Carbon atoms are grey, hydrogen atoms are white, and oxygen atoms are red. [C–H···π] distance (Å) and angle (deg): 2.75, 134.34.

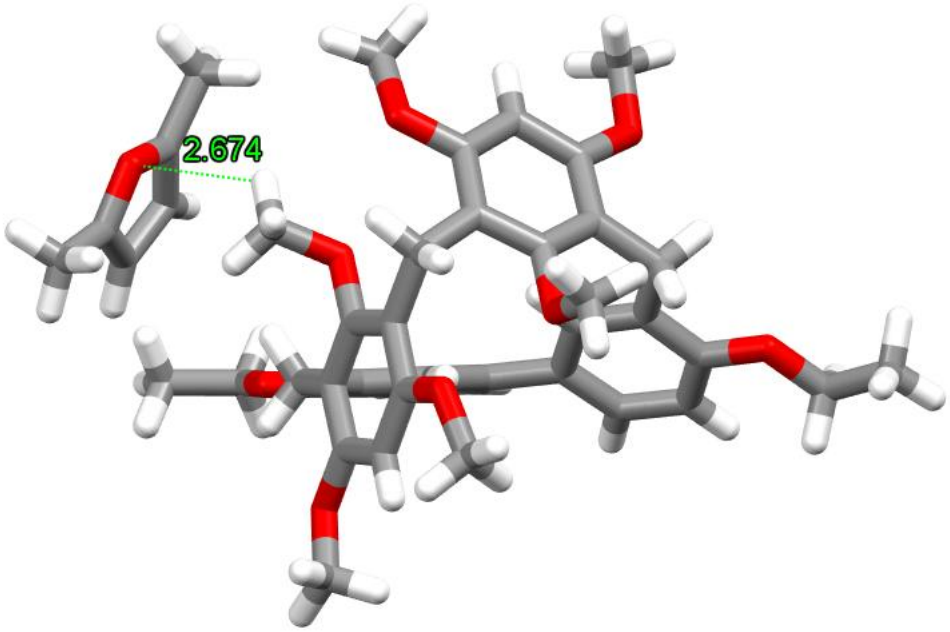


Fig. S14. Capped-stick representation of the single crystal structure of **DMeF@HB3**. Carbon atoms are grey, hydrogen atoms are white, and oxygen atoms are red. Hydrogen-bond parameters: [C···O] distances (Å), [H···O] distances (Å) and [C–H···O] angles (deg) of [C–H···O] hydrogen bonds, 3.22, 2.67, 115.17.

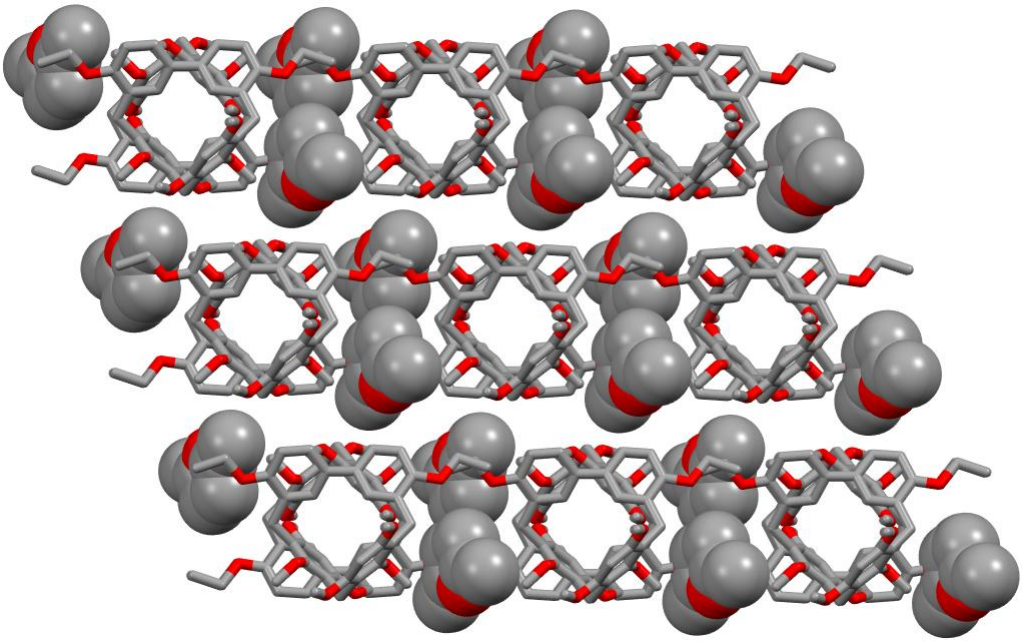


Fig. S15. Capped-stick and spacefill representation of the single crystal structure of **DMeF@HB3** in a packing mode. Carbon atoms are grey and oxygen atoms are red. Hydrogen atoms are omitted for clarity.

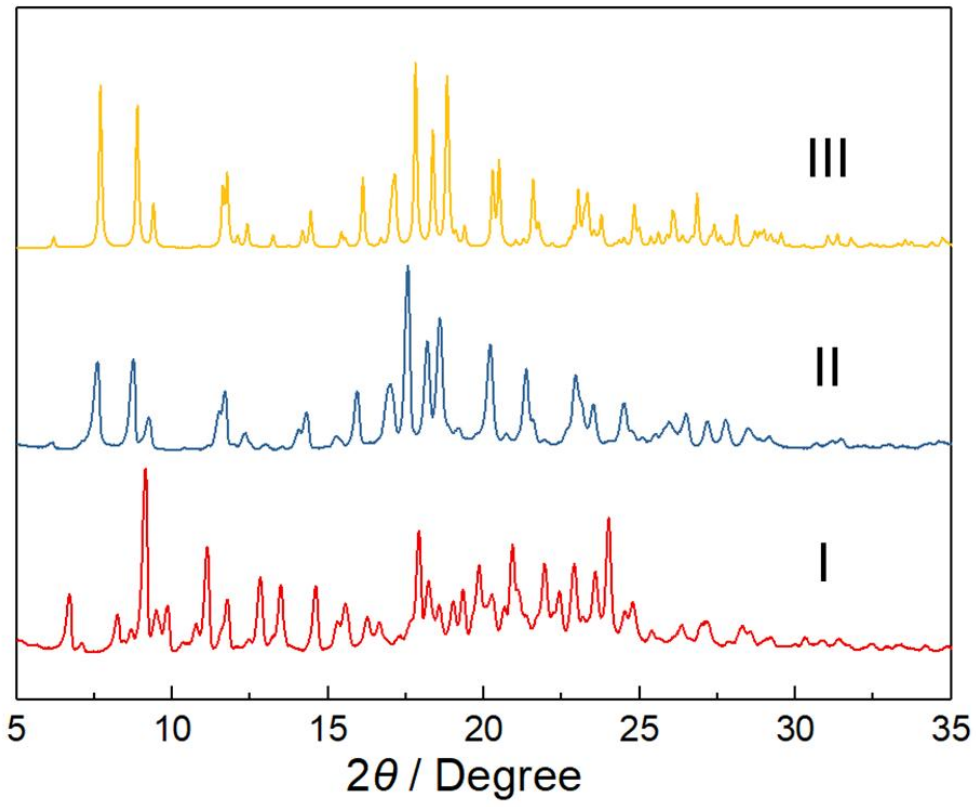


Fig. S16. PXRD patterns of **HB3**: (I) activated **HB3***α*; (II) after adsorption of **DMeF** vapor; (III) simulated from single crystal structure of **DMeF@HB3**.

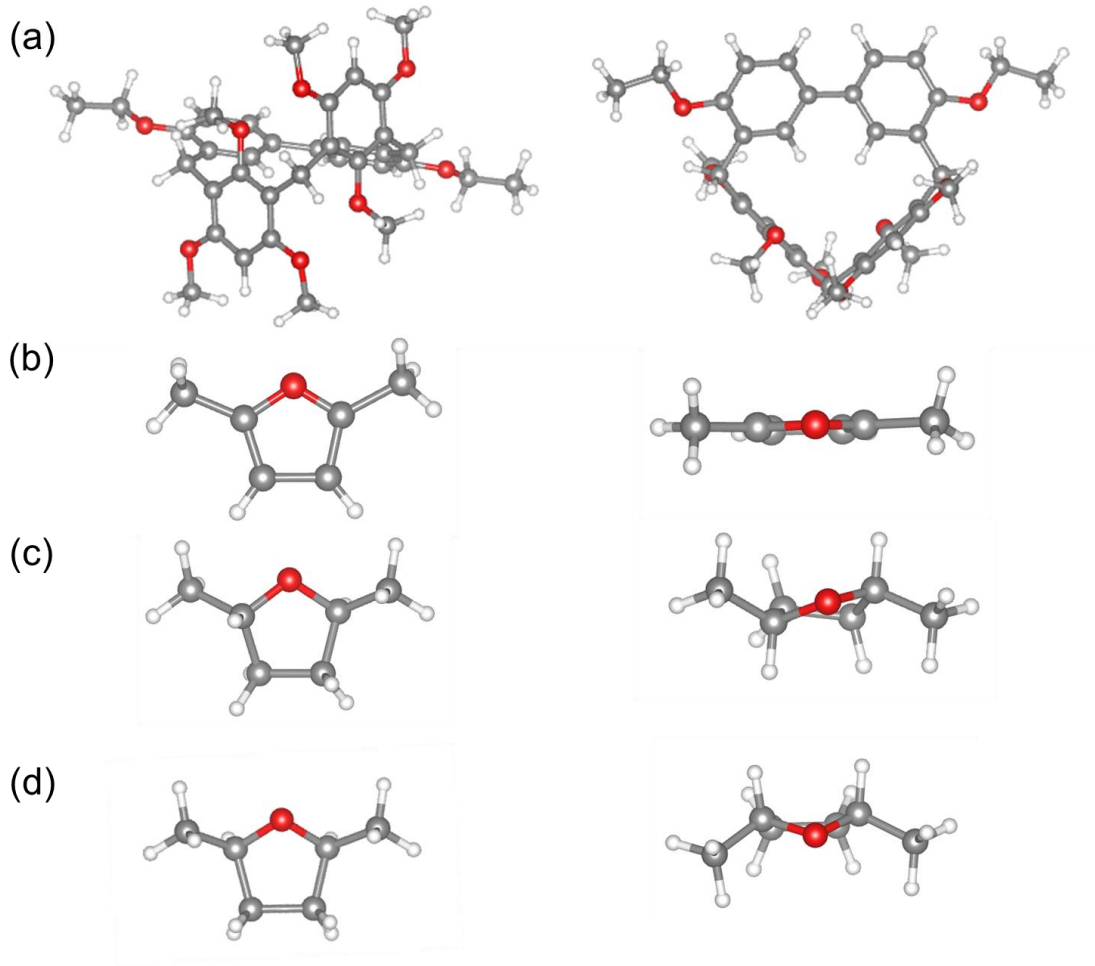


Fig. S17. The optimized structures of (a) **HB3**, (b) **DMeF**, (c) *trans*-**DMeTHF** and (d) *cis*-**DMeTHF**.

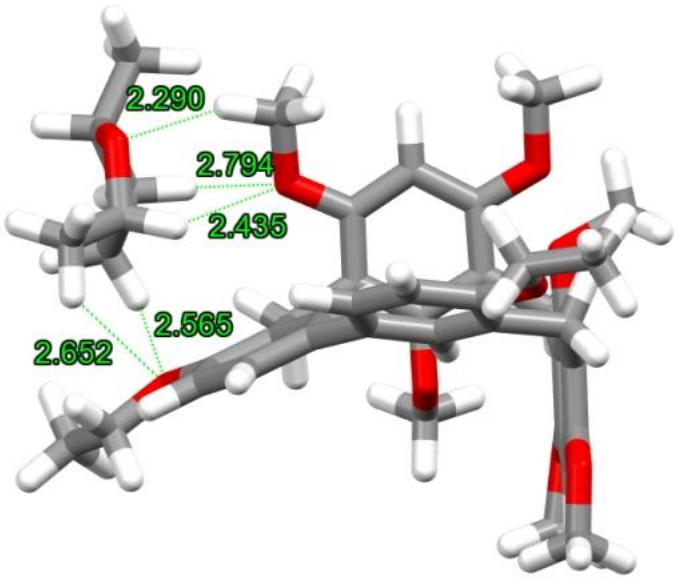


Fig. S18. Capped-stick representation of the calculated structure of *trans*-**DMeTHF@HB3**. Carbon atoms are grey, hydrogen atoms are white, and oxygen atoms are red. Hydrogen-bond parameters: [C···O] distances (Å), [H···O] distances (Å) and [C–H···O] angles (deg) of [C–H···O] hydrogen bonds, 3.25, 2.29, 145.60; 3.61, 2.79, 131.33; 3.29, 2.44, 133.07; 3.33, 2.57, 126.63; 3.46, 2.65, 130.09.

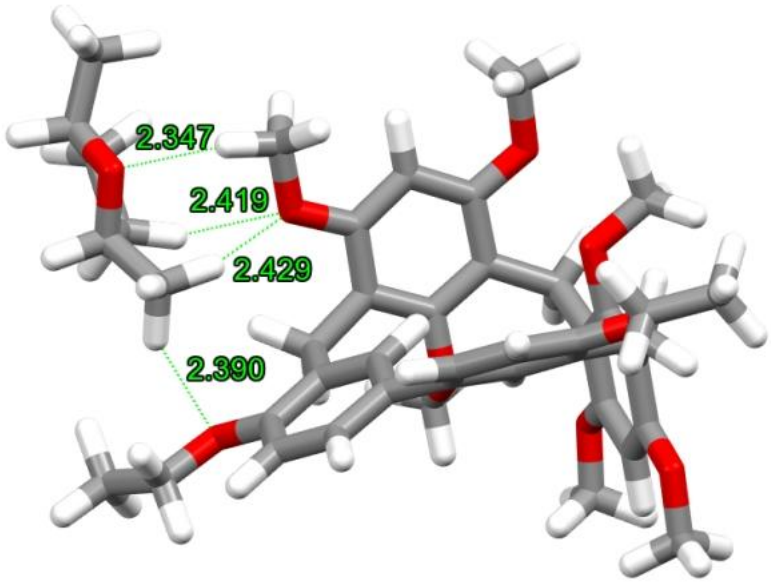


Fig. S19. Capped-stick representation of the calculated structure of *cis*-**DMeTHF@HB3**. Carbon atoms are grey, hydrogen atoms are white, and oxygen atoms are red. Hydrogen-bond parameters: [C···O] distances (Å), [H···O] distances (Å) and [C–H···O] angles (deg) of [C–H···O] hydrogen bonds, 3.42, 2.35, 166.01; 3.38, 2.42, 145.22; 3.39, 2.43, 145.83; 3.36, 2.39, 147.49.

Table S3. Calculated binding energies of **DMeF**/**DMeTHF** in **HB3**.

Substance	Number of guest molecules in **HB3**	E_{BE} (kJ/mol)
DMeF	1	−33.98
trans-**DMeTHF**	1	−30.75
cis-**DMeTHF**	1	−28.24

4.3. DMeF and DMeTHF Mixture Adsorption Experiments

For each mixture solid–vapor experiment, an open 5.00 mL vial containing 20.00 mg of guest-free **HB3***α* adsorbent was placed in a sealed 20.00 mL vial containing 1.00 mL of a 50:50 *v/v* **DMeF** and **DMeTHF** mixture. The relative uptake amount of **MeF** or **DMeF** in **HB3***α* was measured by heating the crystals to release the adsorbed vapor

using GC method. Before measurement, the crystals were heated at 60 ℃ to remove the surface-physically adsorbed vapor.

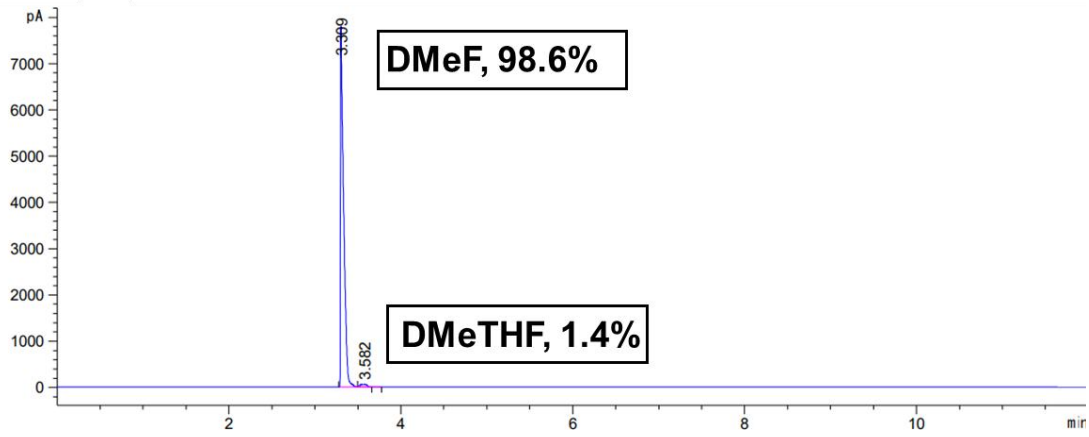


Fig. S20. GC measurements of the relative uptake of **DMeF**/**DMeTHF** in **HB3***α* after 20.00 mg of crystals were put in 1 mL of a 50:50 *v*/*v* **DMeF**/**DMeTHF** mixture for 30 hours.

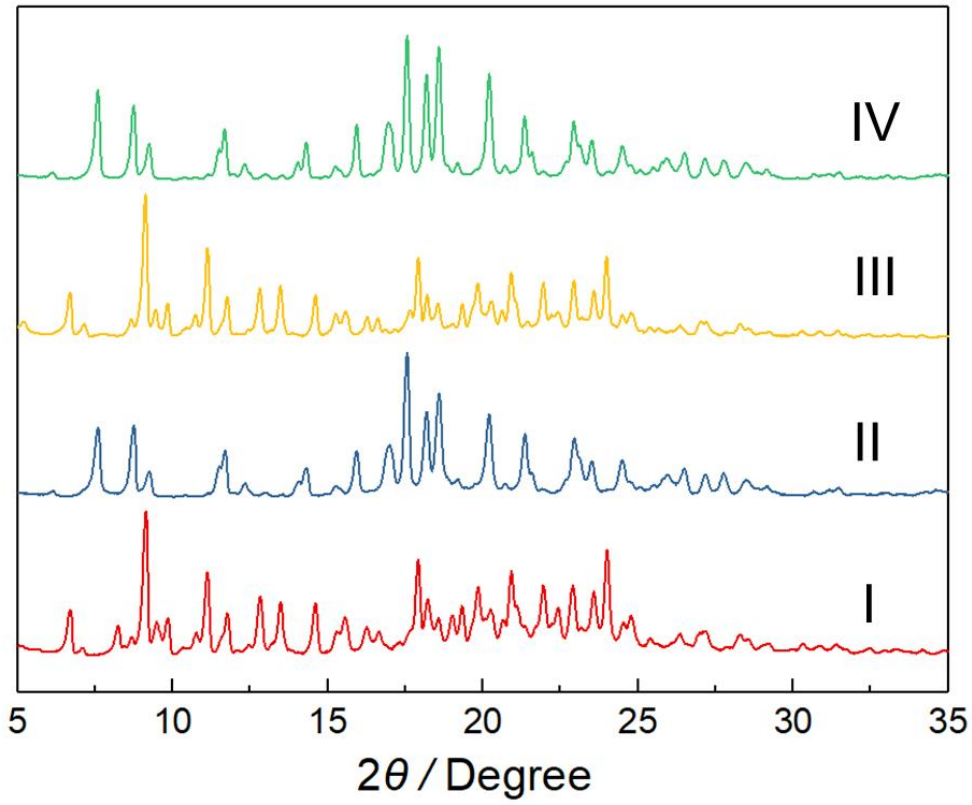


Fig. S21. PXRD patterns of **HB3**: (I) activated **HB3***α*; (II) after adsorption of **DMeF** vapor; (III) after adsorption of **DMeTHF** vapor; (IV) after adsorption of a 50:50 *v*/*v* **DMeF** and **DMeTHF** mixture vapor.

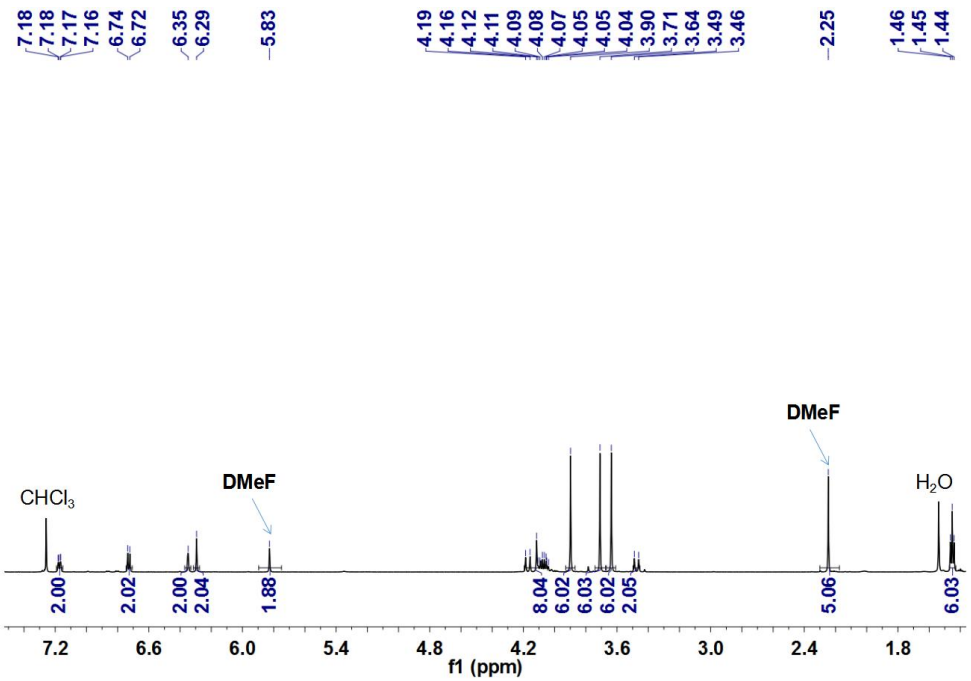


Fig. S22. ^{1}H NMR spectrum (600 MHz, chloroform-*d*, 298 K) of **HB3***α* after adsorption of a 50:50 *v/v* **MeF** and **DMeTHF** mixture vapor.

5. Recycling Experiments of Hybrid[3]arene

An open 5.00 mL vial containing 20.00 mg of **DMeF@HB3** was desolvated under vacuum at 150 ℃ overnight. The resultant crystals were characterized by TGA, PXRD and ^{1}H NMR methods.

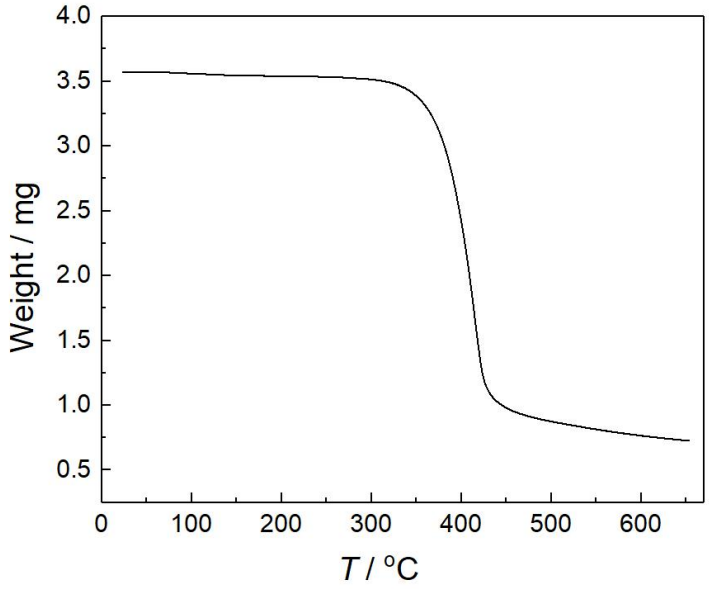


Fig. S23. TGA curve of **DMeF@HB3** after removal of **DMeF**.

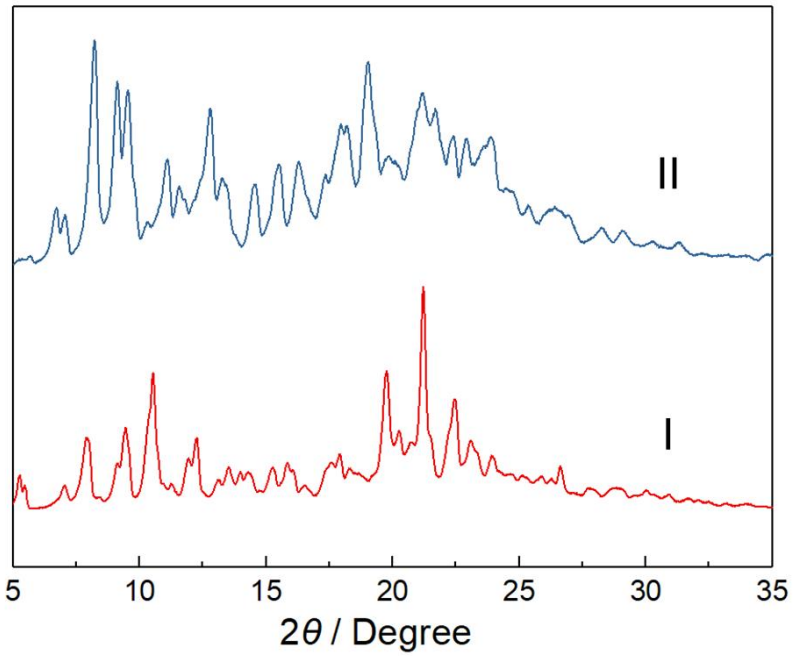


Fig. S24. PXRD patterns of **HB3**: (I) **HB3***α*; (II) desolvated **DMeF@HB3**. This result indicated that **DMeF@HB3** could transform back to activated **HB3***α* after removal of **DMeF**.

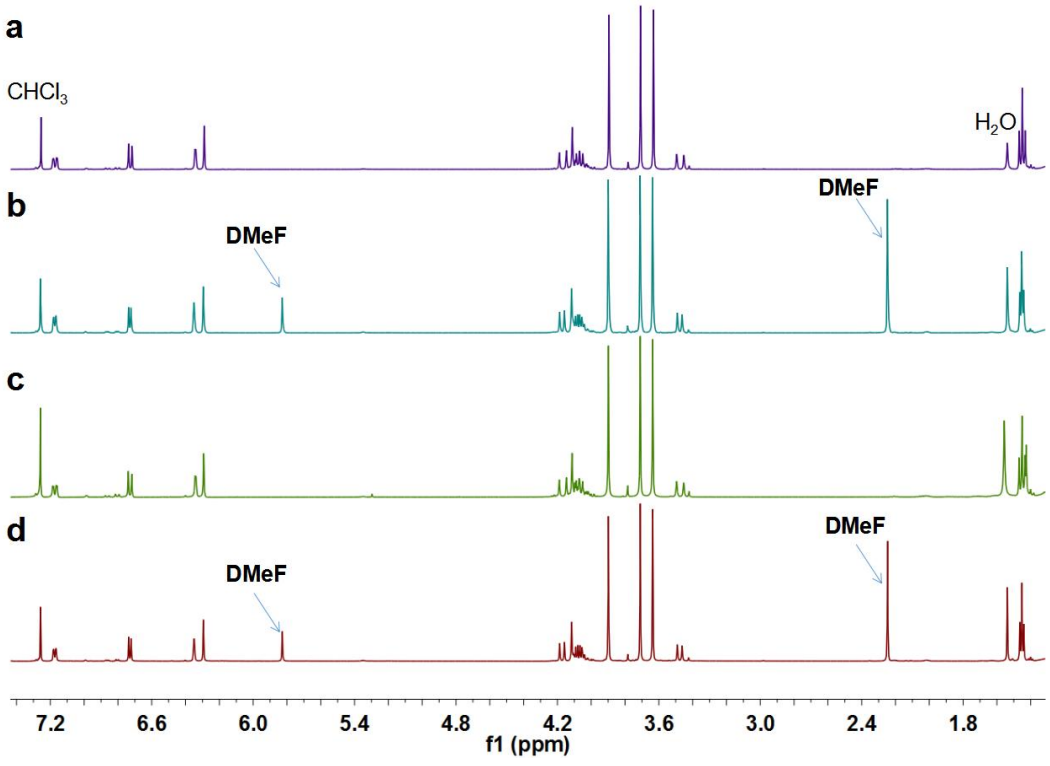


Fig. S25. ^{1}H NMR spectra (400 MHz, chloroform-*d*, 298 K): (a) original **HB3***α*; (b) **HB3***α* after adsorption of **DMeF** vapor; (c) **DMeF@HB3** after removal of **DMeF**; (d) desolvated **DMeF@HB3** after adsorption of **DMeF** vapor.

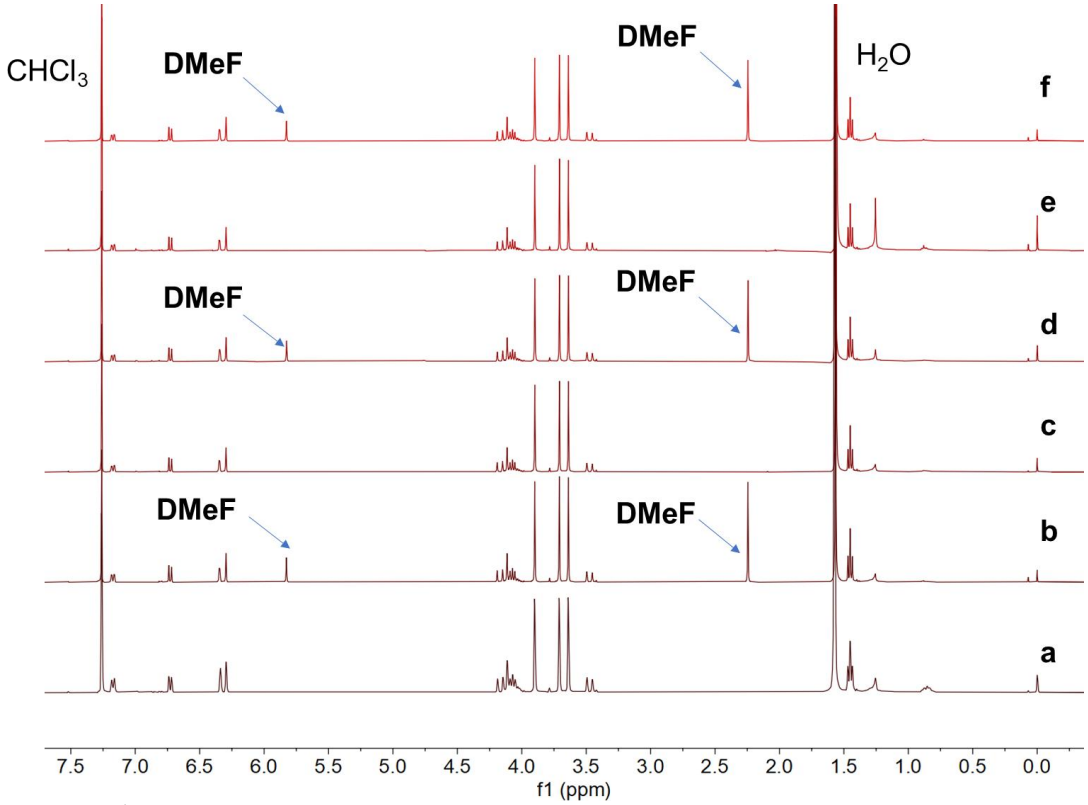


Fig. S26. ^{1}H NMR spectra (400 MHz, chloroform-d, 298 K): (a) original **HB3***α*; (b) **HB3***α* after adsorption of **DMeF** vapor; (c) **DMeF@HB3** after removal of **DMeF** with five cycles; (d) desolvated **DMeF@HB3** after adsorption of **DMeF** vapor with five cycles; (e) **DMeF@HB3** after removal of **DMeF** with ten cycles; (f) desolvated **DMeF@HB3** after adsorption of **DMeF** vapor with ten cycles.

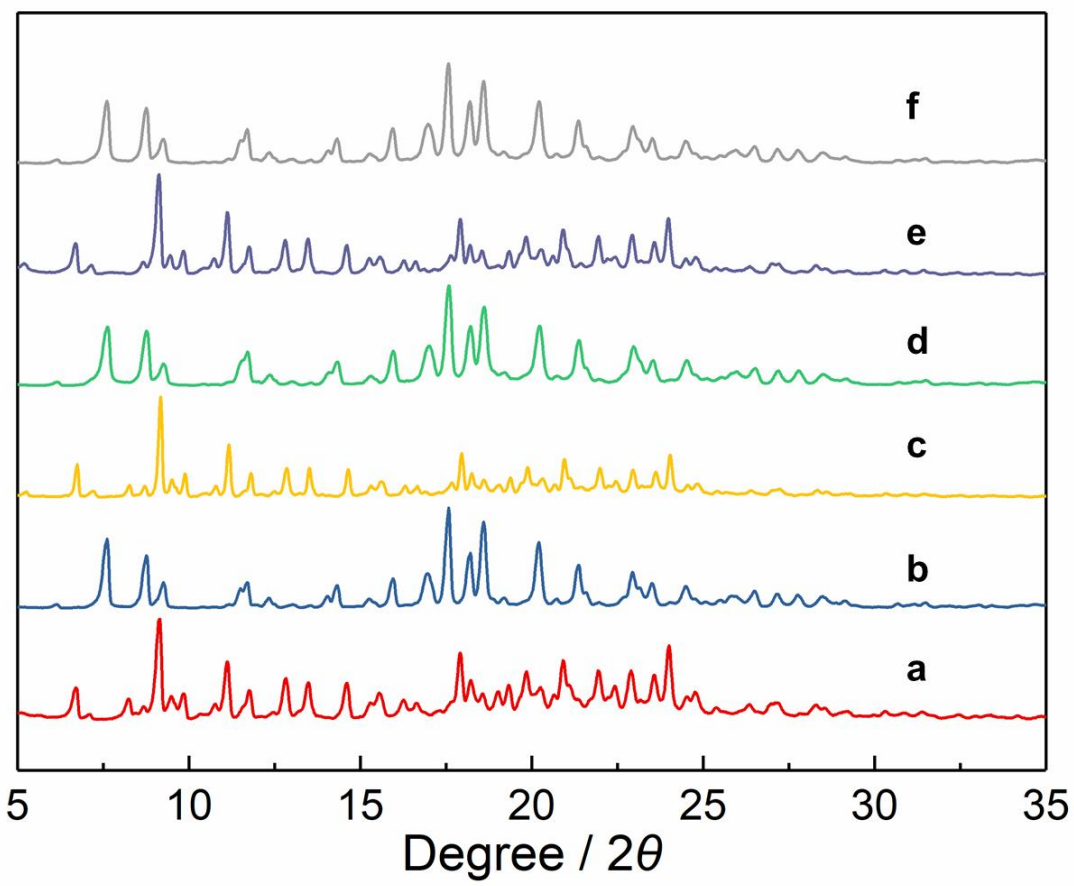


Fig. S27. PXRD patterns of **HB3**: (a) original **HB3***α*; (b) **HB3***α* after adsorption of **DMeF** vapor; (c) **DMeF@HB3** after removal of **DMeF** with five cycles; (d) desolvated **DMeF@HB3** after adsorption of **DMeF** vapor with five cycles; (e) **DMeF@HB3** after removal of **DMeF** with ten cycles; (f) desolvated **DMeF@HB3** after adsorption of **DMeF** vapor with ten cycles.

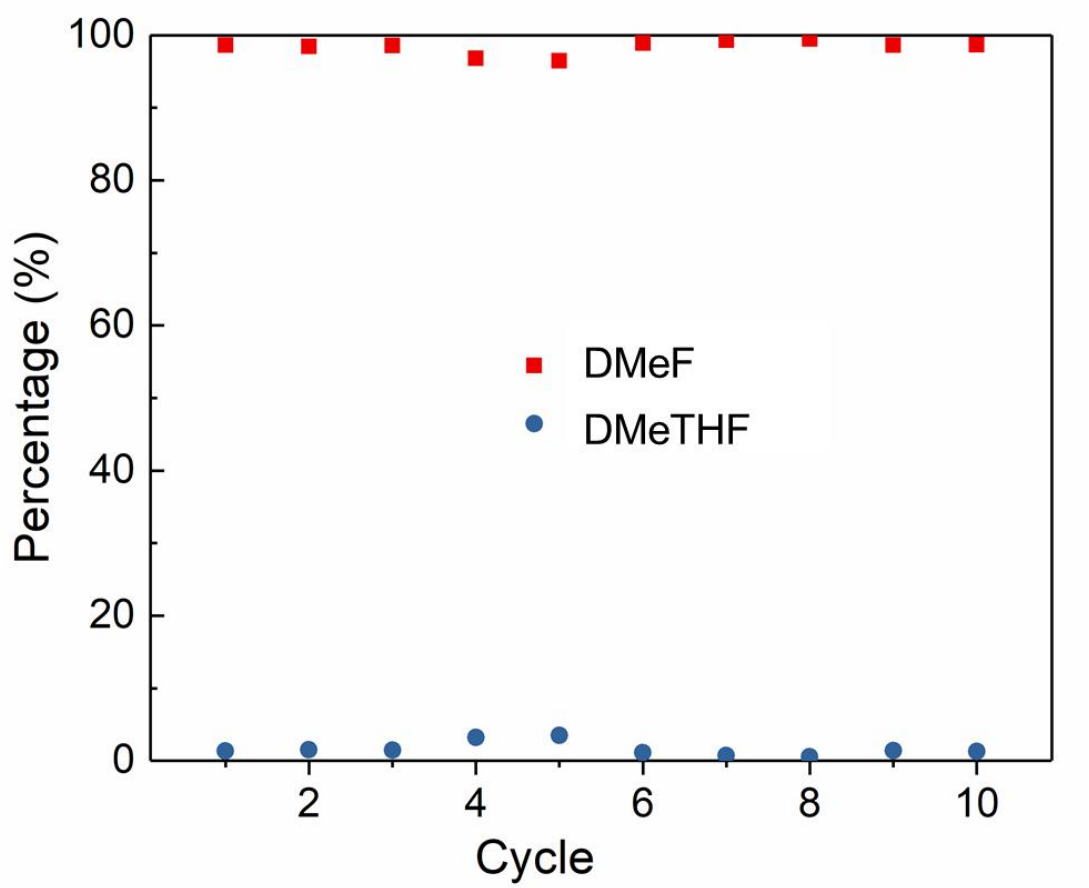


Fig. S28. Relative uptake of **DMeF** and **DMeTHF** by **HB3***α* over 30 hours after **HB3***α* was recycled ten times.

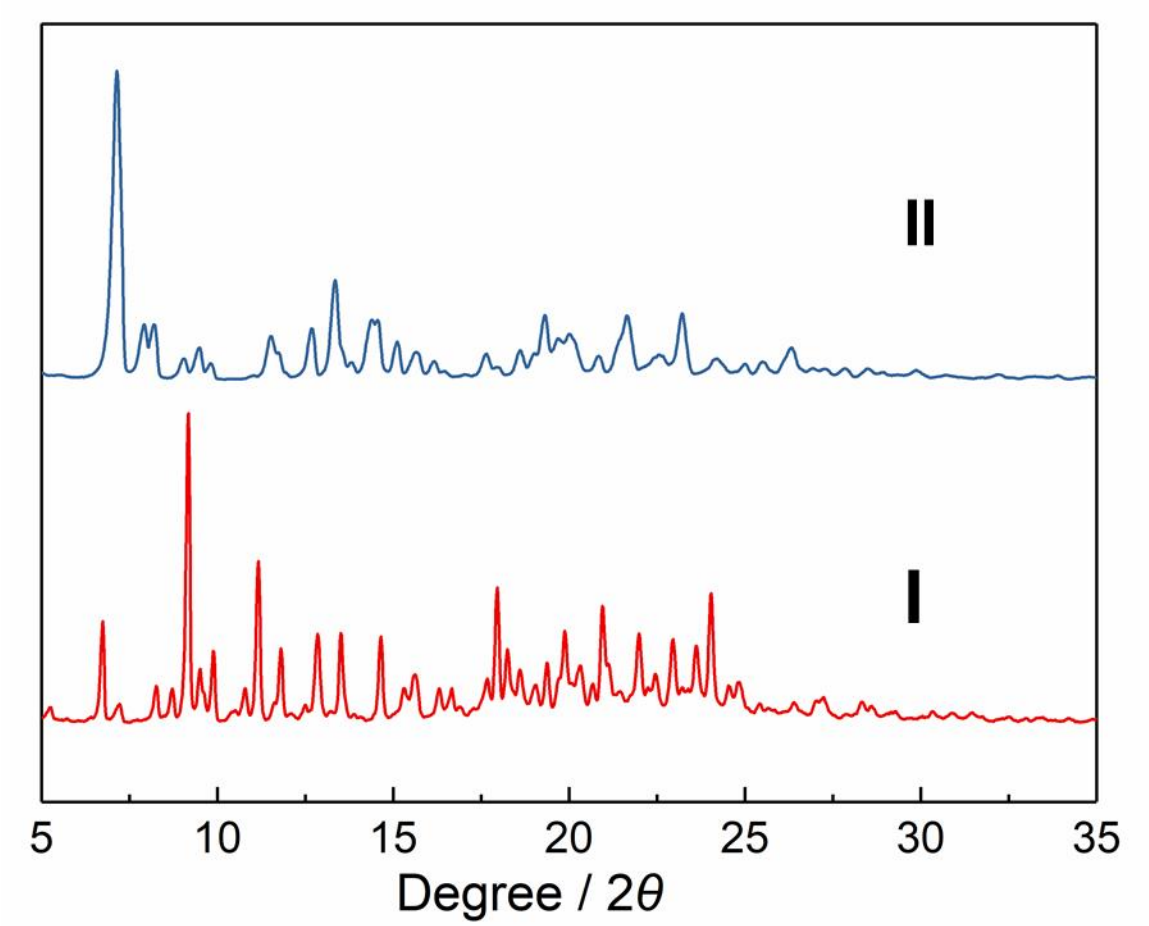


Fig. S29. PXRD patterns of **HB3**: (I) activated **HB3**; (II) initial synthetic **HB3**.

6. References

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