Supporting Information (52 pages)

Perfect separation of benzene and toluene associated with vapochromic behaviors by hybrid[4]arene-based co-crystals

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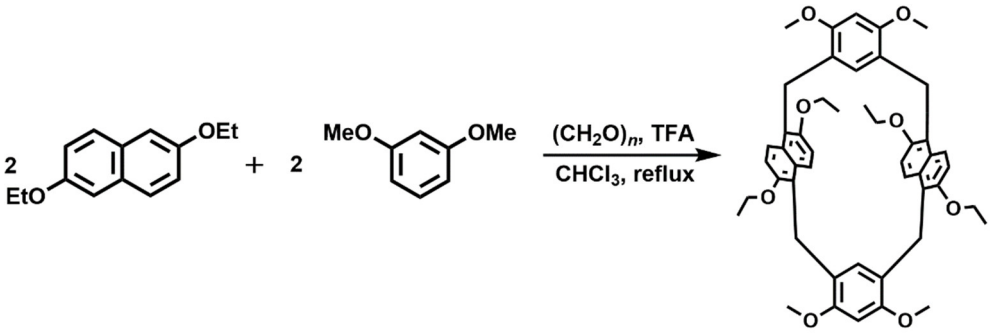
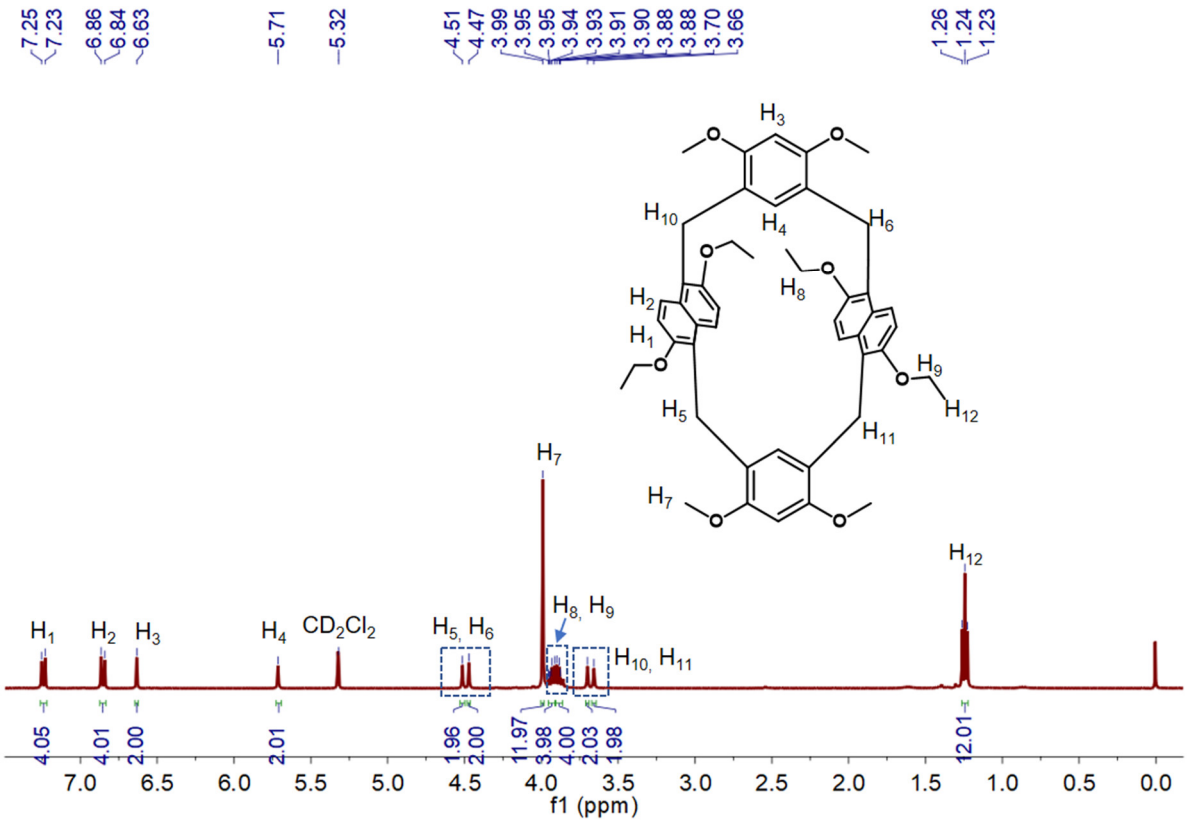
1. Synthesis of hybrid[4]arene

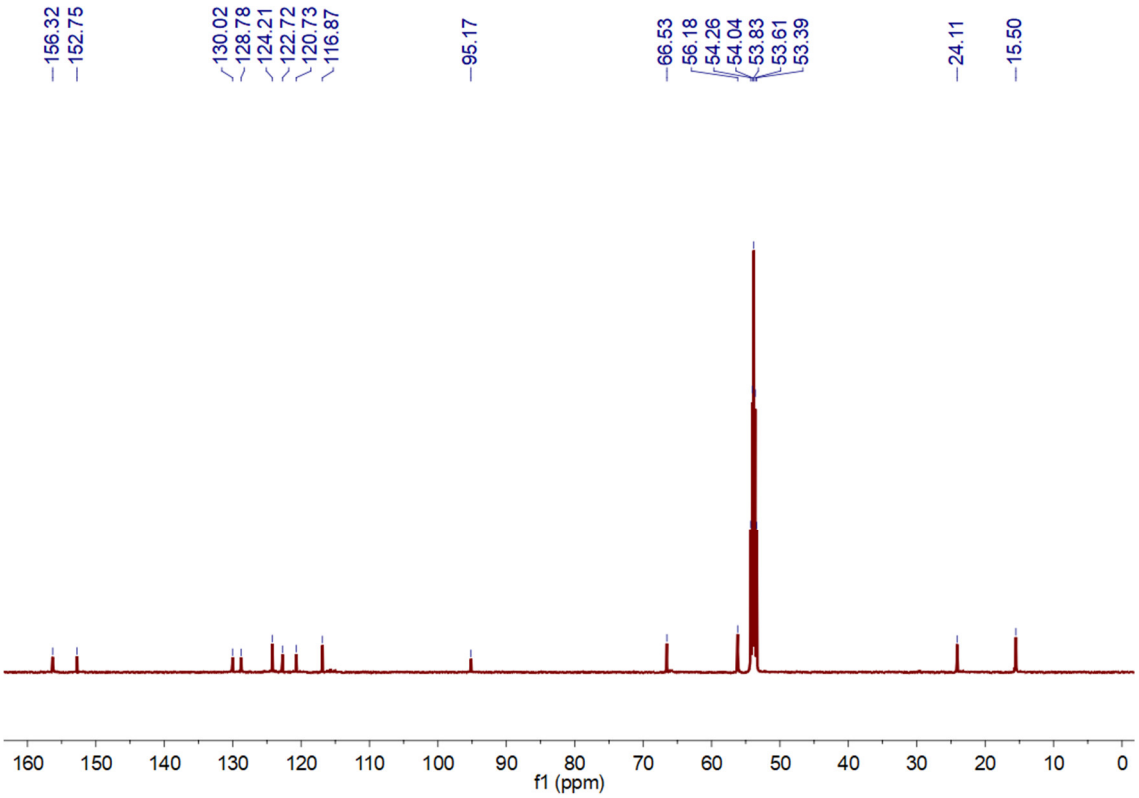
Supplementary Scheme 1. Synthetic Route to Hybrid[4]arene **H**



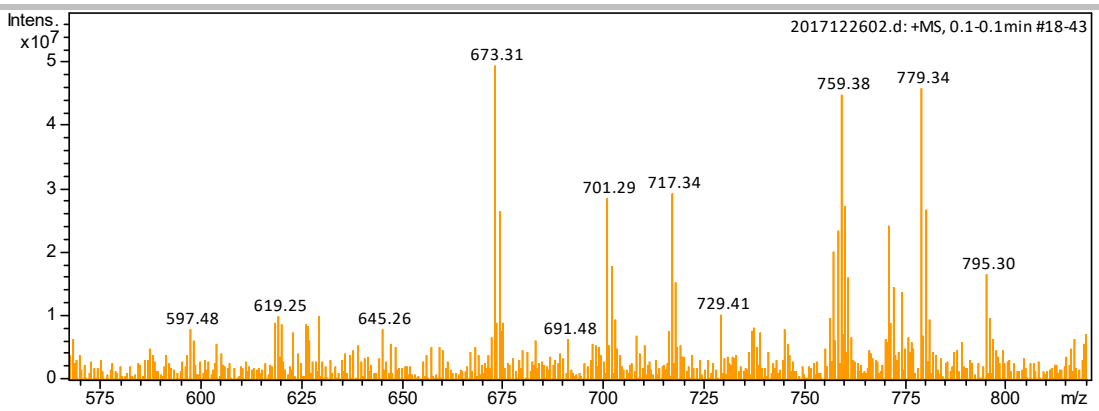
Synthesis of hybrid[4]arene (H): To the solution of 2,6-diethoxylnaphthalene (2.16 g, 10.0 mmol) and 1,3-dimethoxybenzene (1.38 g, 20.0 mmol) in $CHCl_3$ (200 mL), paraformaldehyde (0.600 g, 30.0 mmol) and TFA (10.0 mL) were added. The mixture was refluxed for 35 min. After the reaction was finished, a saturated aqueous solution of 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* 2:1) to get hybrid[4]arene (**H**) as a white solid (3.78 g, 50%), mp: 240-241 °C. The ^{1}H NMR spectrum of **H** is shown in Supplementary Figure 1. ^{1}H NMR (500 MHz, CD_2Cl_2, 293 K) δ (ppm): 7.24 (d, J = 10 Hz, 4H), 6.85 (d, J = 10 Hz, 4H), 6.63 (s, 2H), 5.71 (s, 2H), 4.51 (s, 2H), 4.47 (s, 2H), 3.99 (s, 12H), 3.95–3.93 (m, 4H), 3.91–3.88 (m, 4H), 3.70 (s, 2H), 3.66 (s, 2H), 1.24 (t, J = 15 Hz, 12H). The ^{13}C NMR spectrum of **H** is shown in Supplementary Figure 2. ^{13}C NMR (125 MHz, CD_2Cl_2, 293 K) δ (ppm): 156.32, 152.75, 130.02, 128.78, 124.21, 122.72, 120.73, 116.87, 95.17, 66.53, 66.53, 56.18, 54.26, 54.04, 53.83, 53.61, 53.39, 24.11, 15.50.



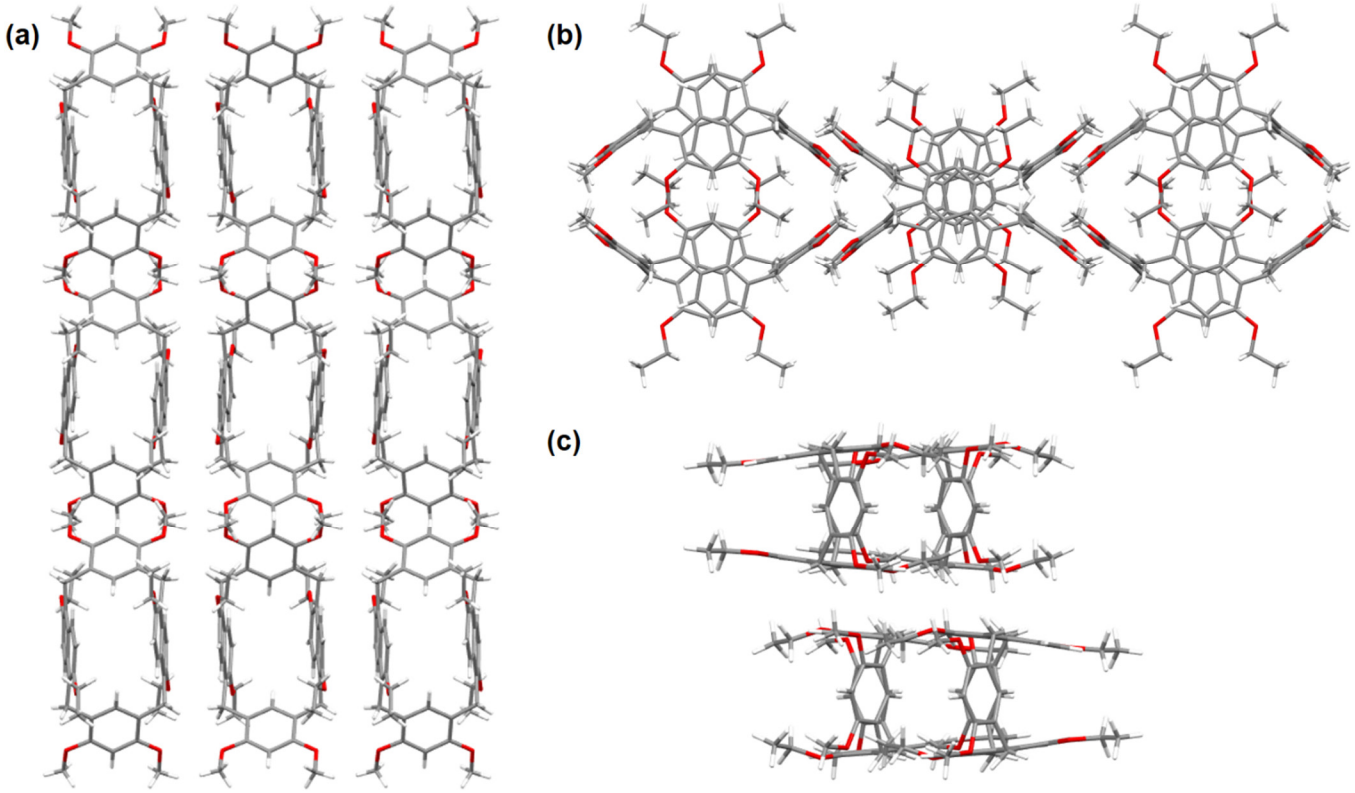
Supplementary Figure 1. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H**.



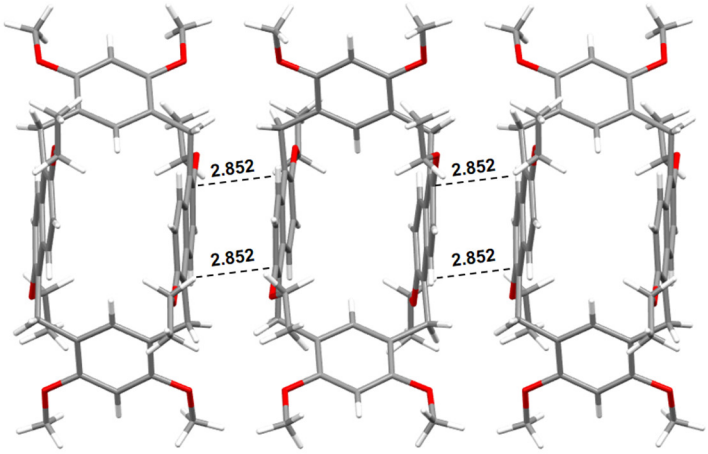
Supplementary Figure 2. ^{13}C NMR spectrum (125 MHz, CD_2Cl_2, 293 K) of **H**.



Supplementary Figure 3. Electrospray ionization mass spectrum of **H**. Assignment of main peaks: *m*/*z* 779.34 $[M + Na]^+$, 795.30 $[M + K]^+$.

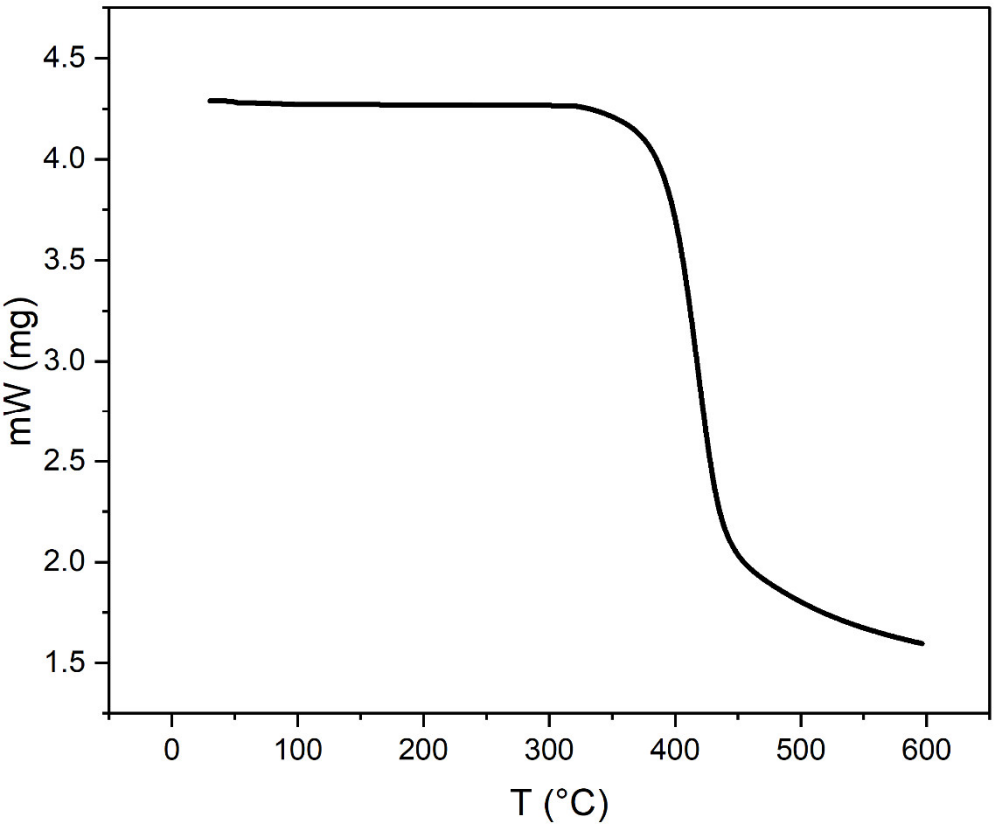


Supplementary Figure 4. Three views of the crystal packing structure of **H**. (a) *a*-axi, (b) *b*-axi and (c) *c*-axi.

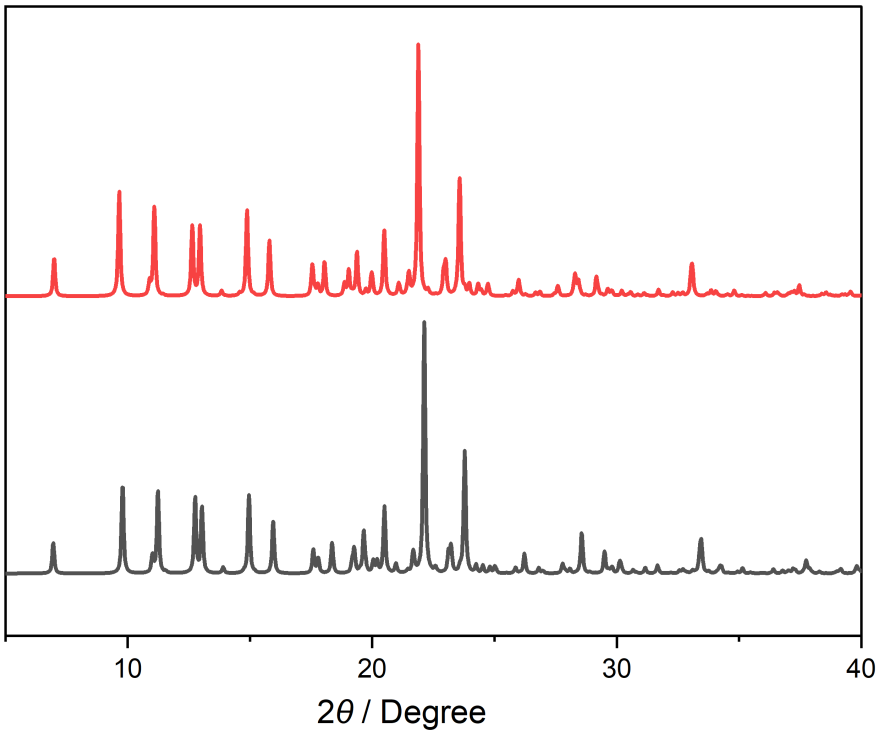


Supplementary Figure 5. H was arranged parallel to its neighbor **H** through intermolecular C–H···π interactions. C–H···π distance: 2.852 Å.

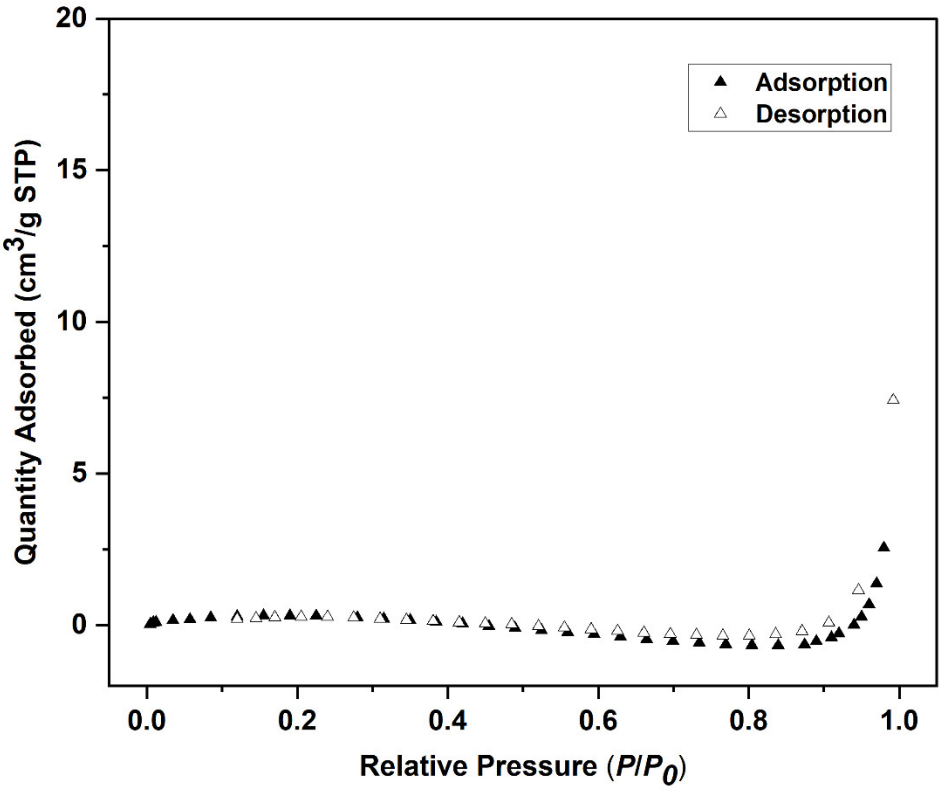
Supplementary Figure 6. The crystal packing structure of **H** along *b*-axis. **H** was arranged parallel to its neighbor **H** through intermolecular C–H···O interactions. C–H···O distance: 2.671 Å.



Supplementary Figure 7. Thermogravimetric analysis of **H***α*.



Supplementary Figure 8. Powder X-ray diffraction patterns of **H**: black line, original **H***α*; red line, simulated from single crystal structure of **H**.



Supplementary Figure 9. N_2 adsorption-desorption isotherm of **H*α***. The BET surface area value is 0.820 m^2/g. Adsorption, closed symbols; desorption, open symbols.

2. Crystallography data

Supplementary Table 1. Experimental single crystal X-ray data for **H**.

Formula	**H**
Crystallization Solvent	CH_2Cl_2
Collection Temperature (K)	170(2)
Formula	$C_{48}H_{52}O_8$
Formula Weight	756.89
Crystal System	Orthorhombic
Space Group	*Pbcn*
a [Å]	25.3974(9)
b [Å]	9.6581(5)
c [Å]	16.0561(7)
α [o]	90
β [o]	90
γ [o]	90
V [Å^3]	3938.4(3)
Z	4
D_{calcd} [g cm^{-3}]	1.277
Absorption coefficient (mm^{-1})	0.086
F(000)	1616.0
Theta range [º]	4.512 to 54.24
Reflections collected / unique	57861 [R_{int} = 0.0441]
Data / restraints / parameters	4353 / 18 / 267
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0399, wR_2 = 0.1017
R indices (all data)	R_1 = 0.0515, wR_2 = 0.1104
Goodness-of-fit on F^2	1.034
Largest difference peak and hole [e.A^{-3}]	0.21 and -0.17
CCDC	2244801

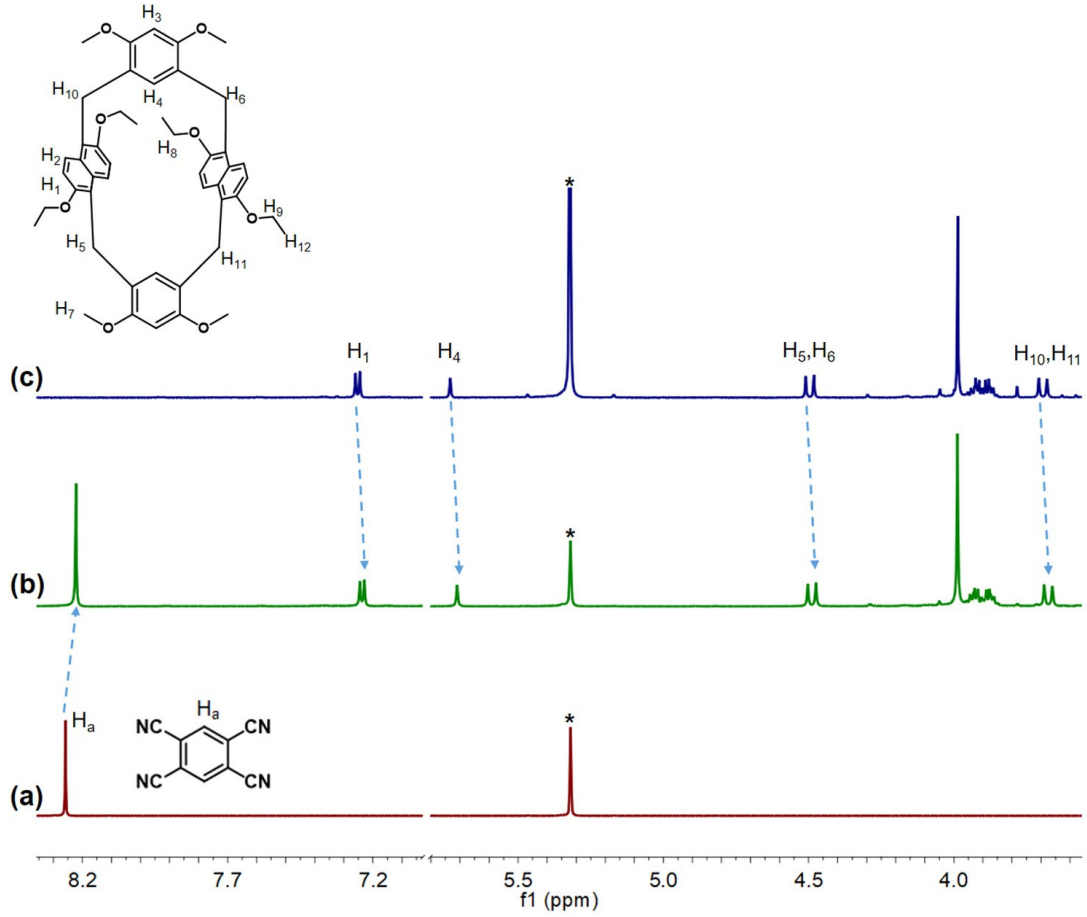
Supplementary Table 2. Experimental single crystal X-ray data for **H-TCNB@CH_2Cl_2**.

Formula	**H-TCNB@CH_2Cl_2**
Crystallization Solvent	CH_2Cl_2
Collection Temperature (K)	273(2)
Formula	$C_{60}H_{58}Cl_4N_4O_8$
Formula Weight	1104.90
Crystal System	Orthorhombic
Space Group	*Fdd2*
a [Å]	26.7226(9)
b [Å]	35.7156(12)
c [Å]	11.5081(4)
α [o]	90
β [o]	90
γ [o]	90
V [$Å^3$]	10983.5(6)
Z	8
D_{calcd} [g cm^{-3}]	1.336
Absorption coefficient (mm^{-1})	0.275
F(000)	4624.0
Theta range [º]	2.95 to 26.40
Reflections collected / unique	13330 / 4718 [R_{int} = 0.0203]
Data / restraints / parameters	4718 / 1 / 347
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0817, wR_2 = 0.0817
R indices (all data)	R_1 = 0.0842, wR_2 = 0.0842
Goodness-of-fit on F^2	1.054
Largest difference peak and hole [$e.A^{-3}$]	0.254 and -0.342
CCDC	2244721

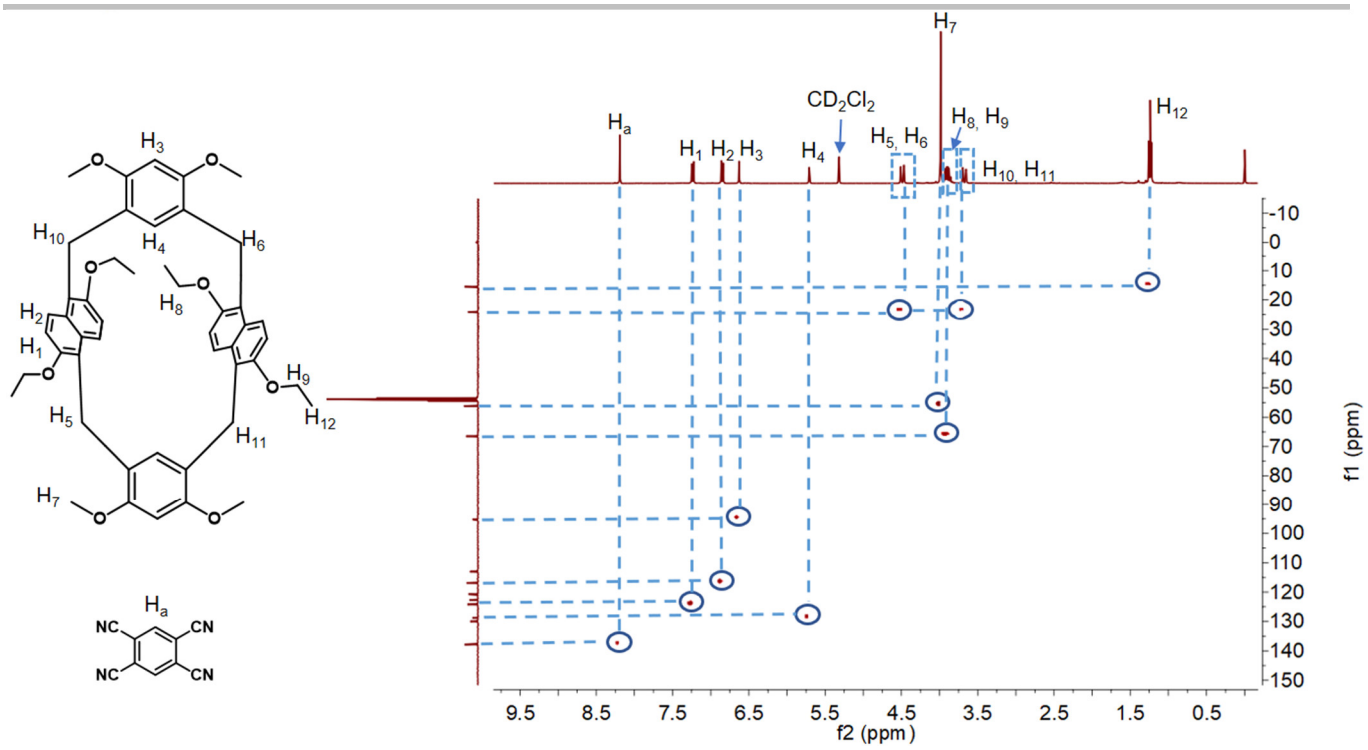
Supplementary Table 3. Experimental single crystal X-ray data for **H-TCNB@Bz**.

Formula	**H-TCNB@Bz**
Crystallization Solvent	benzene
Collection Temperature (K)	170(2)
Formula	$C_{70}H_{66}N_4O_8$
Formula Weight	1091.27
Crystal System	Orthorhombic
Space Group	*Fdd2*
a [Å]	26.4248(8)
b [Å]	36.2735(16)
c [Å]	11.9131(3)
α [o]	90
β [o]	90
γ [o]	90
V [Å^3]	11418.9(7)
Z	8
D_{calcd} [g cm^{-3}]	1.270
Absorption coefficient (mm^{-1})	0.083
F(000)	4624.0
Theta range [º]	4.492 to 54.22
Reflections collected / unique	32095 / 6116 [R_{int} = 0.0415]
Data / restraints / parameters	6116 / 1 / 374
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0323, wR_2 = 0.0323
R indices (all data)	R_1 = 0.0372, wR_2 = 0.0372
Goodness-of-fit on F^2	1.045
Largest difference peak and hole [e.A^{-3}]	0.127 and -0.196
CCDC	2244722

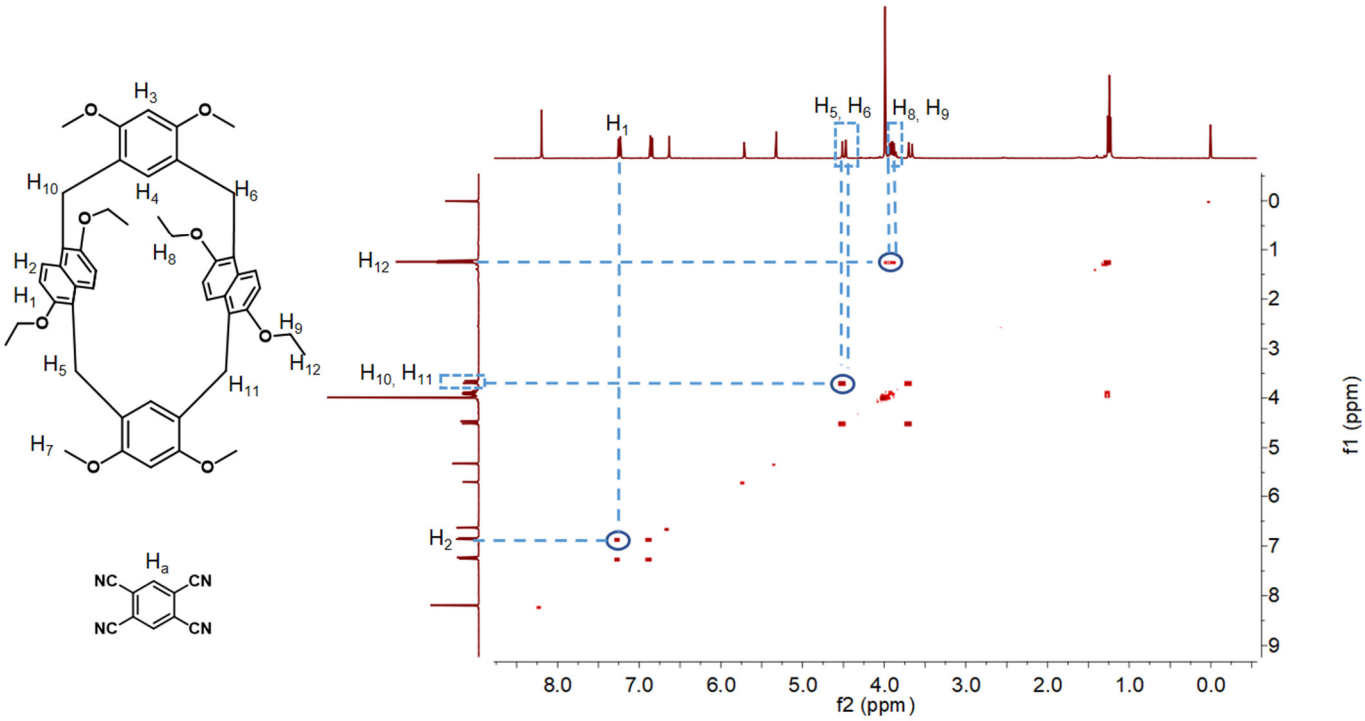
3. Characterization of the complexation of 1,2,4,5-tetracyanobenzene (TCNB) with hybrid[4]arene (H) in solution



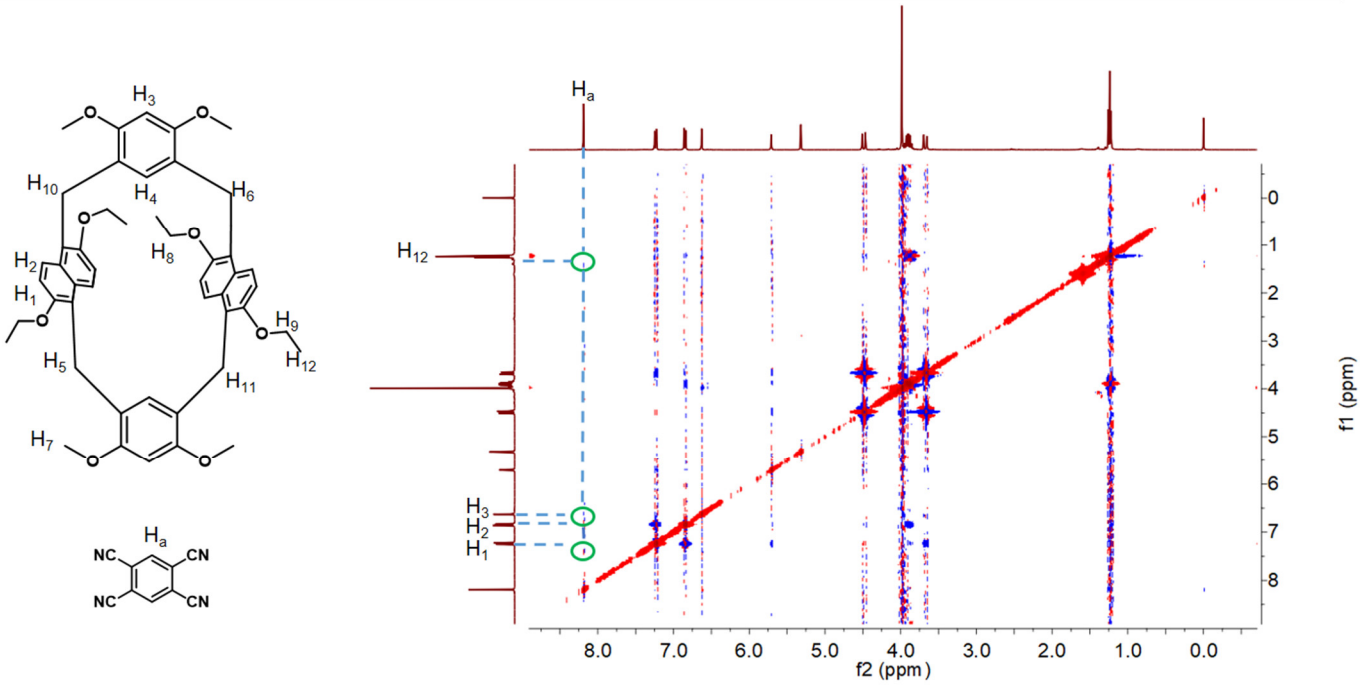
Supplementary Figure 10. Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 293 K) of (a) free **TCNB** (10.0 mM), (b) **H** (10.0 mM) and **TCNB** (10.0 mM), and (c) free **H** (10.0 mM). (*: solvent residues)



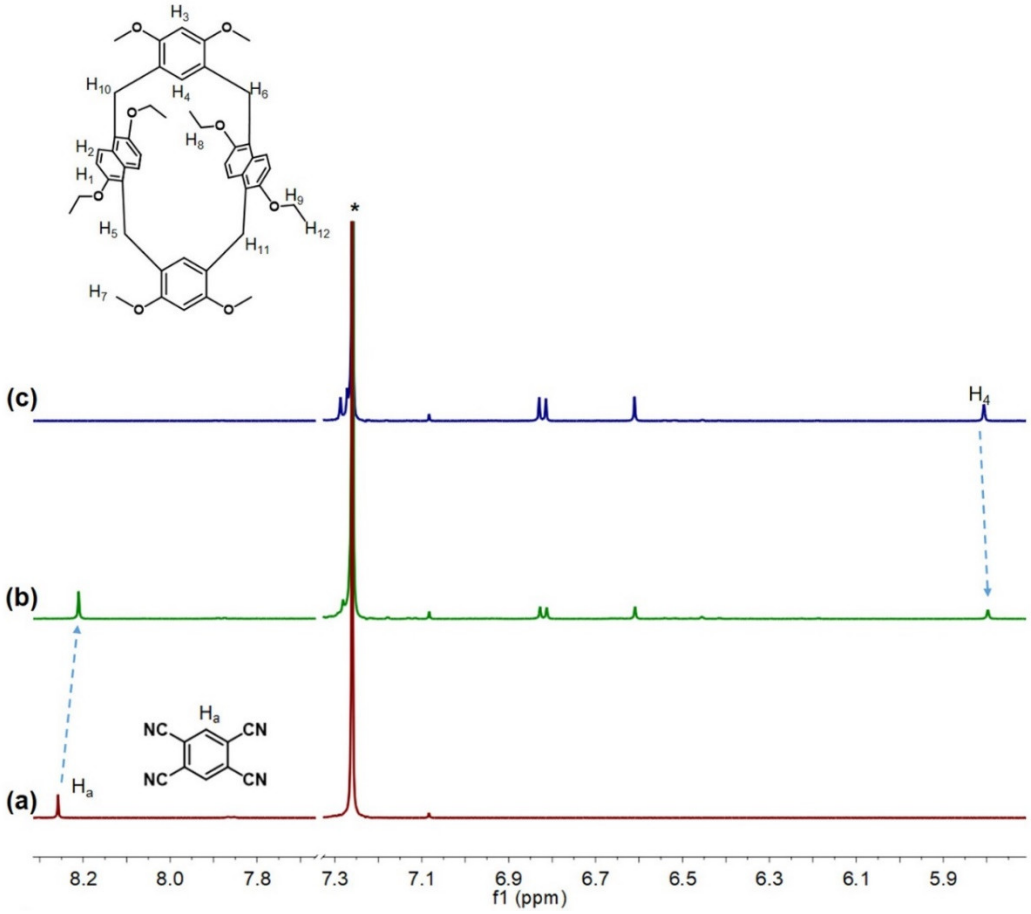
Supplementary Figure 11. HSQC spectrum (500 MHz, CD_2Cl_2, 298 K) of **H** (10.0 mM) with **TCNB** (10.0 mM).



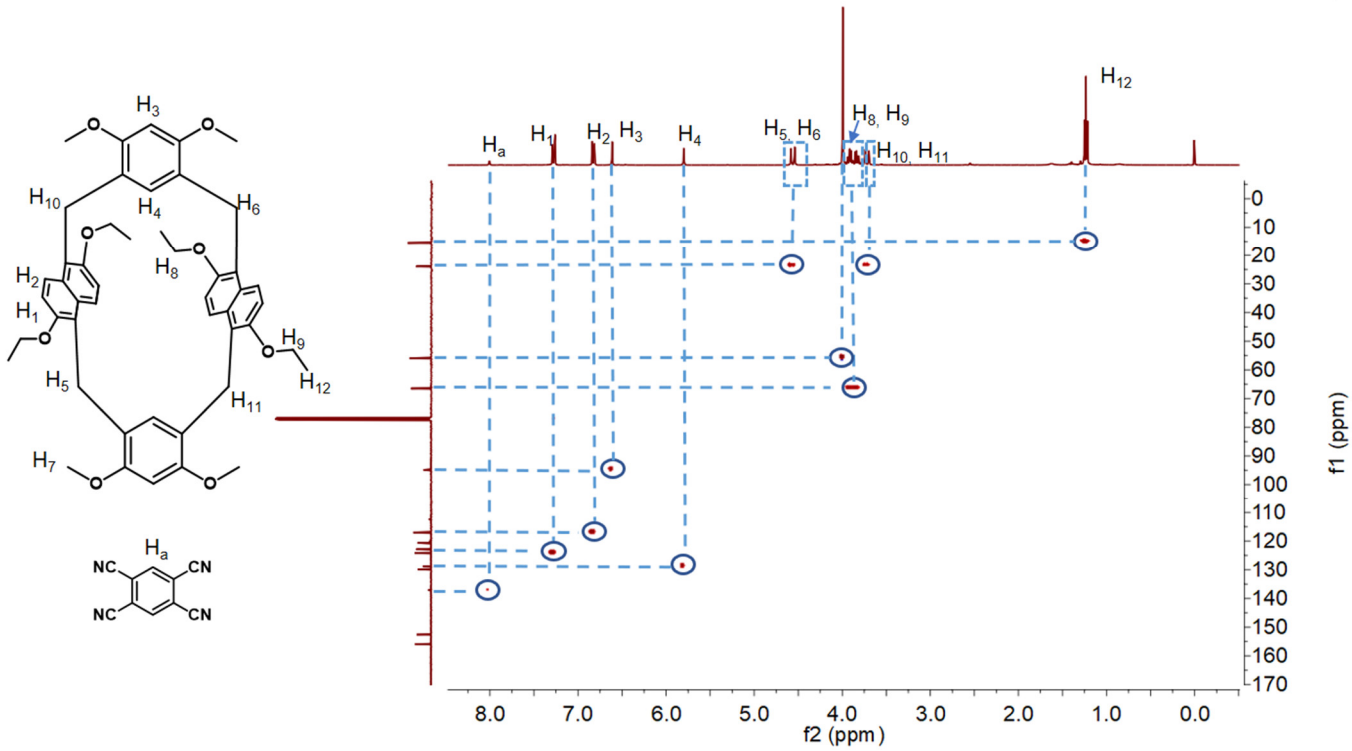
Supplementary Figure 12. 2D COSY spectrum (500 MHz, CD_2Cl_2, 298 K) of **H** (10.0 mM) with **TCNB** (10.0 mM).



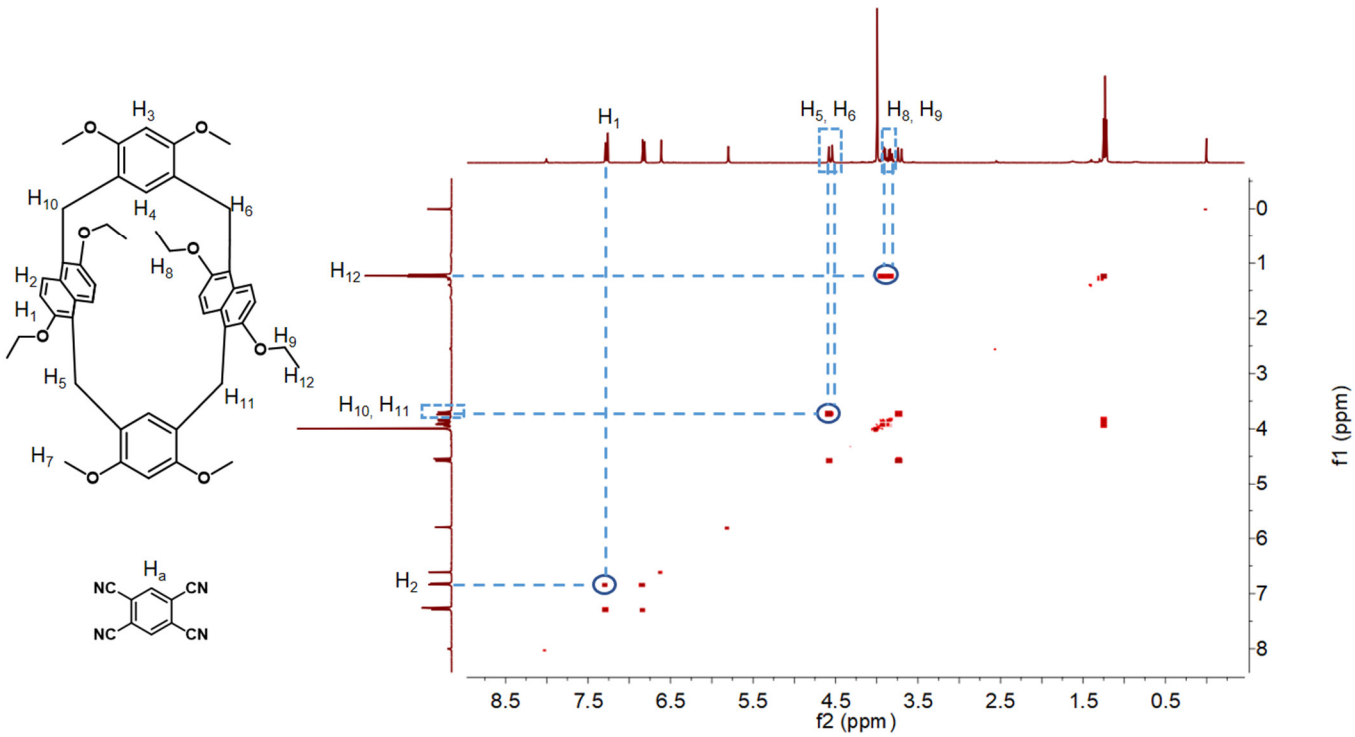
Supplementary Figure 13. 2D NOSEY spectrum (500 MHz, CD_2Cl_2, 298 K) of **H** (10.0 mM) with **TCNB** (10.0 mM).



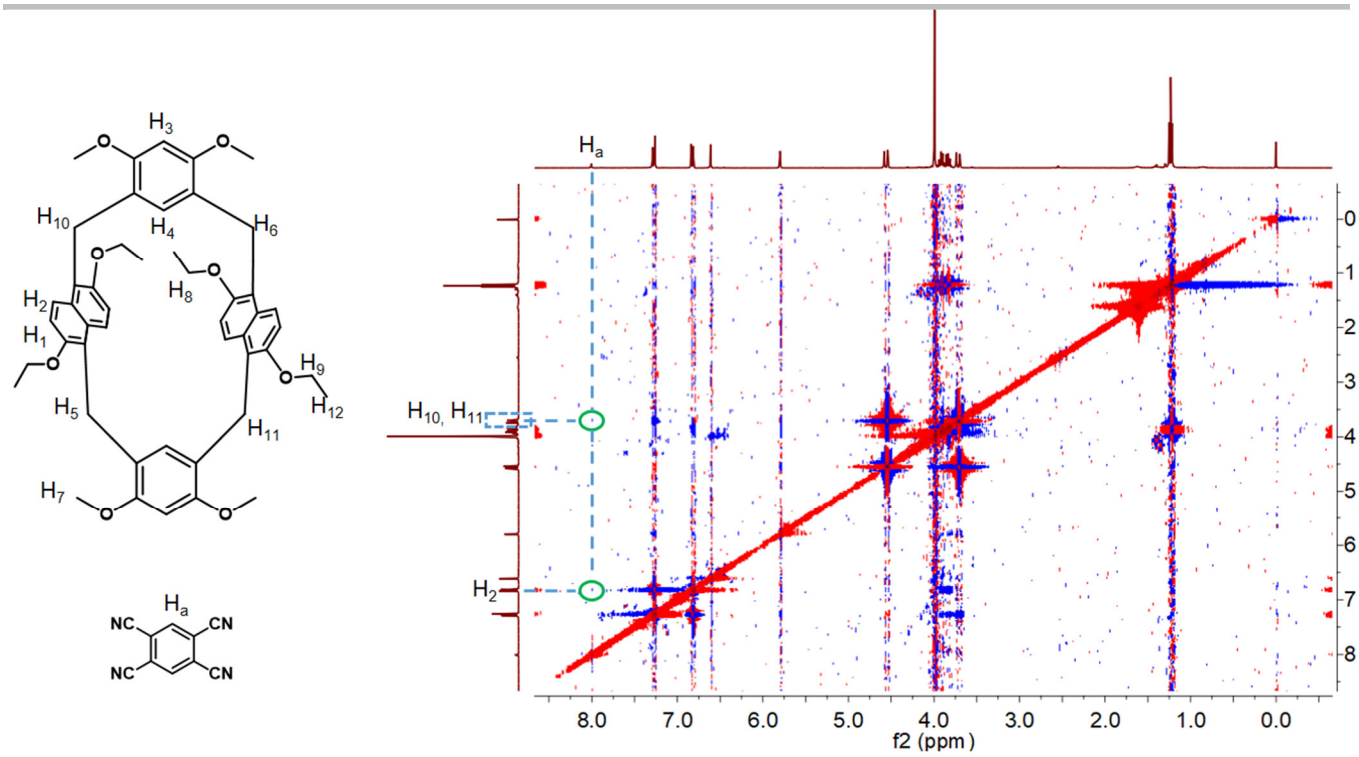
Supplementary Figure 14. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 293 K) of (a) free **TCNB** (10.0 mM), (b) **H** (10.0 mM) and **TCNB** (10.0 mM), and (c) free **H** (10.0 mM). (*: solvent residues)



Supplementary Figure 15. HSQC spectrum (500 MHz, $CDCl_3$, 298 K) of **H** (10.0 mM) with **TCNB** (10.0 mM).

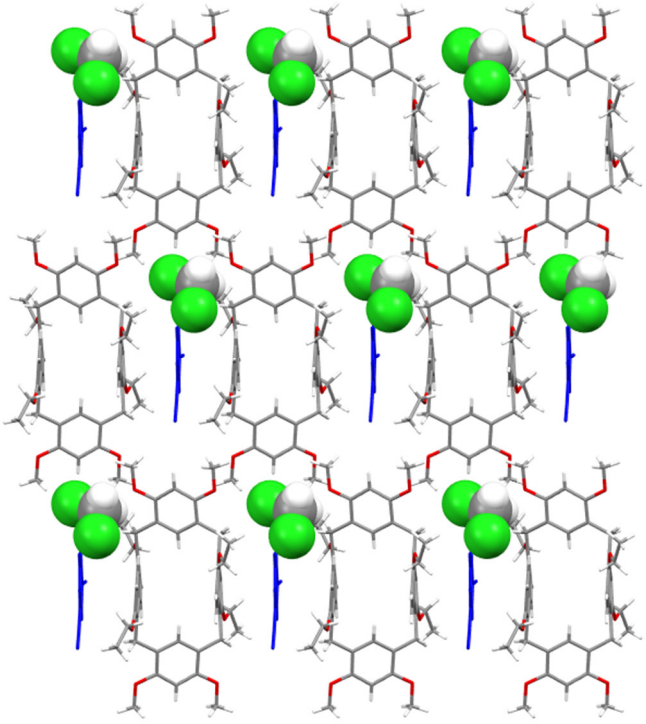


Supplementary Figure 16. 2D COSY spectrum (500 MHz, $CDCl_3$, 298 K) of **H** (10.0 mM) with **TCNB** (10.0 mM).

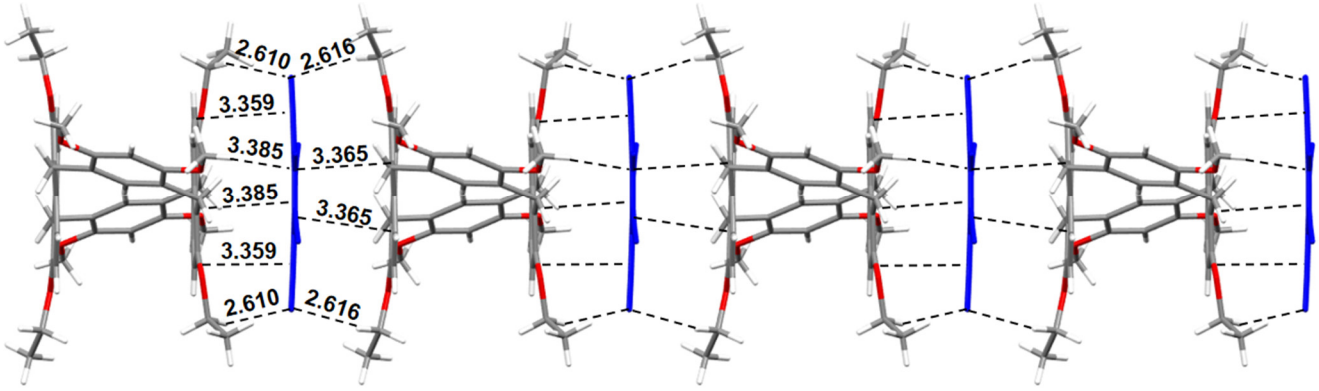


Supplementary Figure 17. 2D NOSEY spectrum (500 MHz, $CDCl_3$, 298 K) of **H** (10.0 mM) with **TCNB** (10.0 mM).

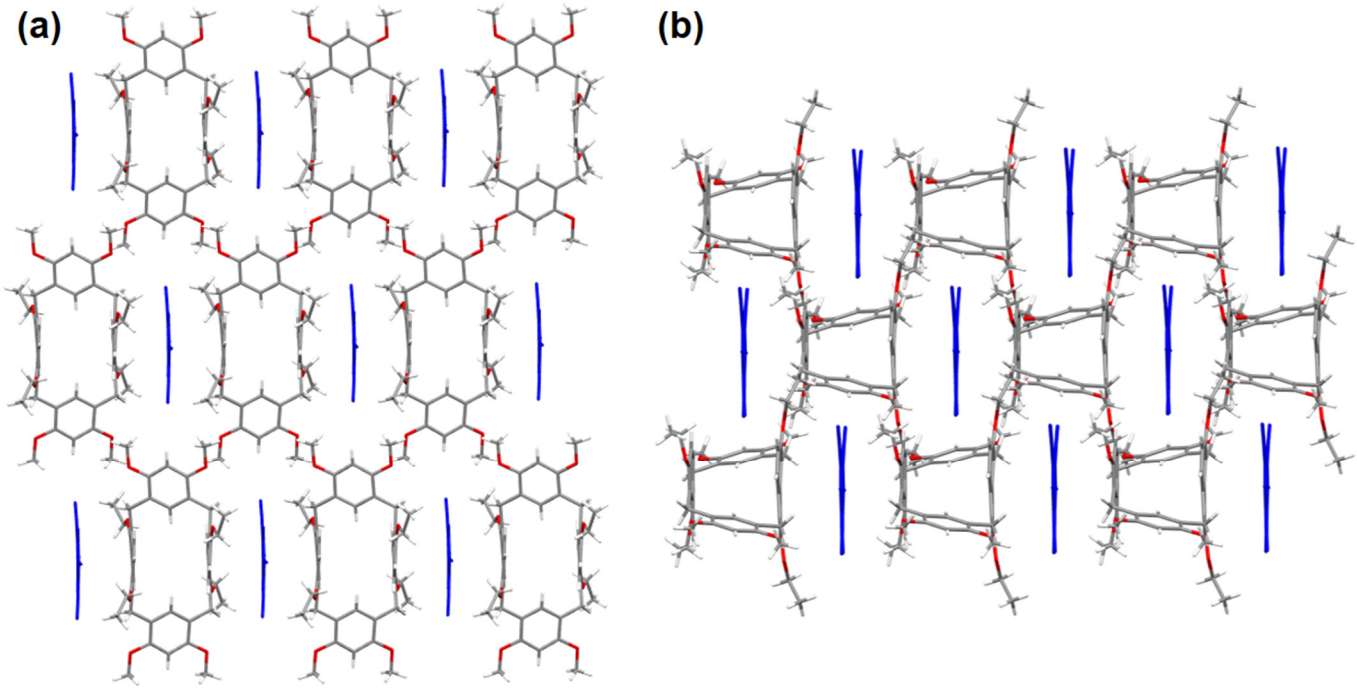
4. Non-covalent interaction analysis in single crystal structure of H-TCNB@CH_2Cl_2



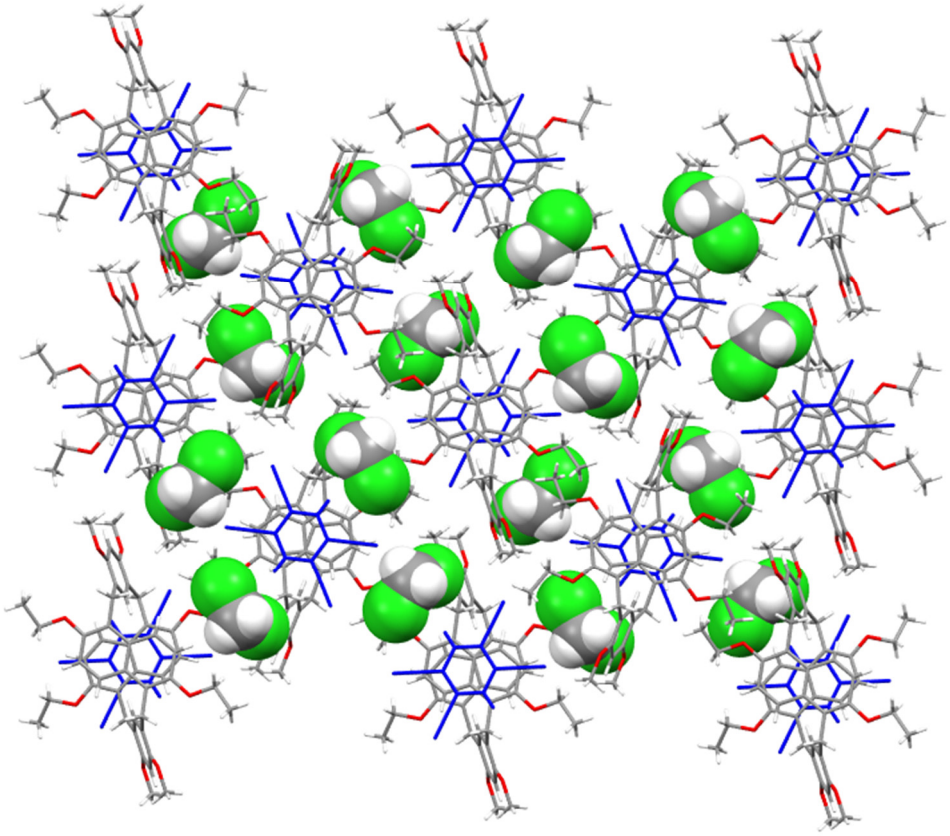
Supplementary Figure 18. Illustration of the packing model of **H-TCNB**@CH_2Cl_2.



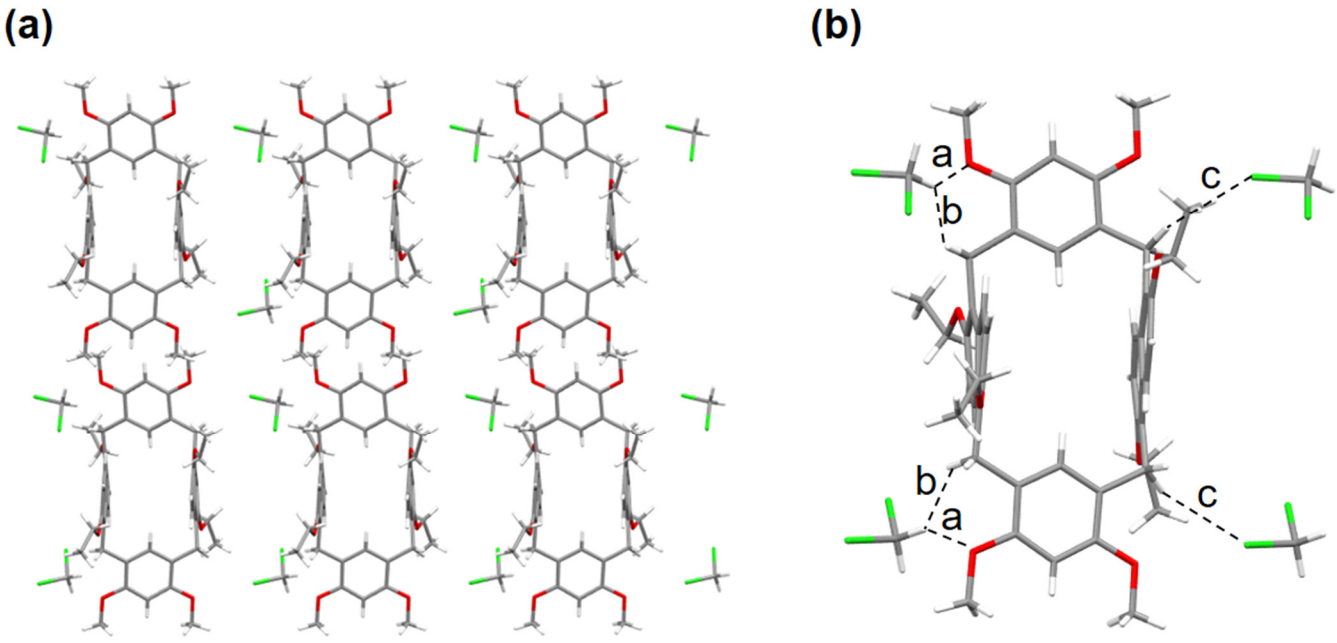
Supplementary Figure 19. The exo-wall π–π interaction between **H** and **TCNB** in the co-crystal structures of **H-TCNB**@CH_2Cl_2. The CH_2Cl_2 molecules are omitted for clarity.



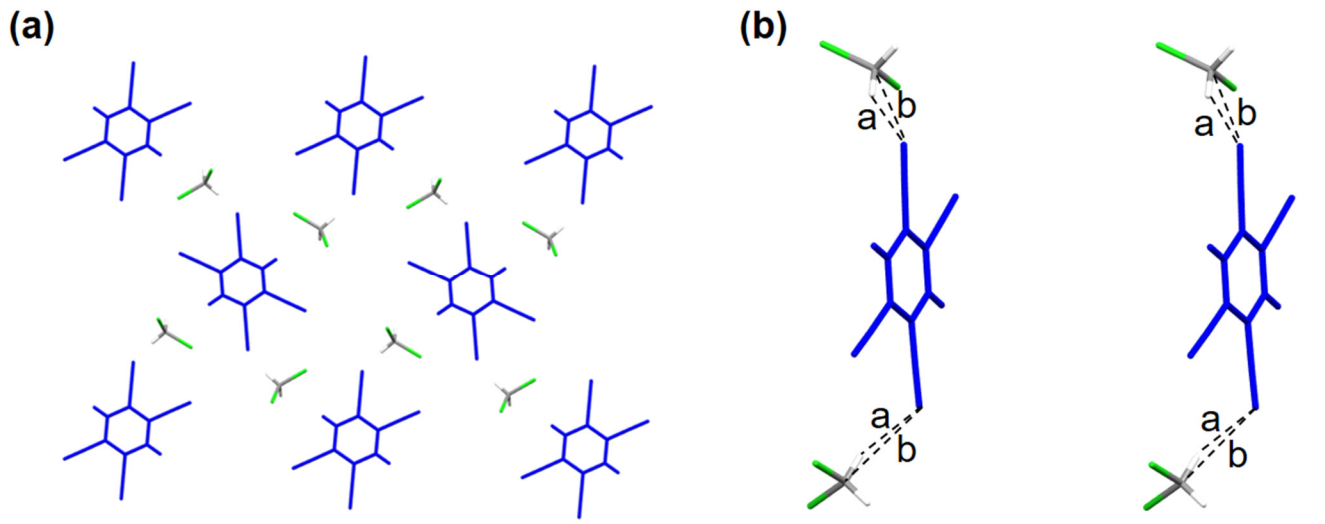
Supplementary Figure 20. Illustration of the packing model of **H-TCNB**@CH_2Cl_2. (a) Side view, (b) Top view. The CH_2Cl_2 molecules are omitted for clarity.



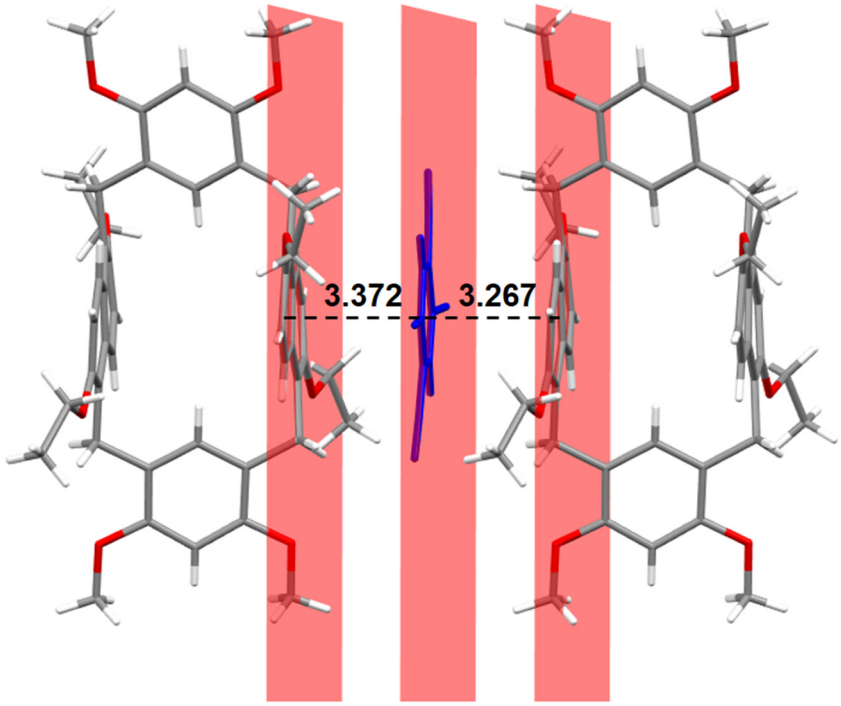
Supplementary Figure 21. Illustration of the packing model of **H-TCNB**@CH_2Cl_2 along *a*-axis.



Supplementary Figure 22. Illustration of the (a) packing model of **H-TCNB**@CH_2Cl_2 and (b) C–H···O and C–H···Cl interactions between CH_2Cl_2 and **H**. The **TCNB** molecules are omitted for clarity. C–H···O distances: a = 2.419 Å, b = 2.343 Å. C–H···Cl distance: c = 2.936 Å.

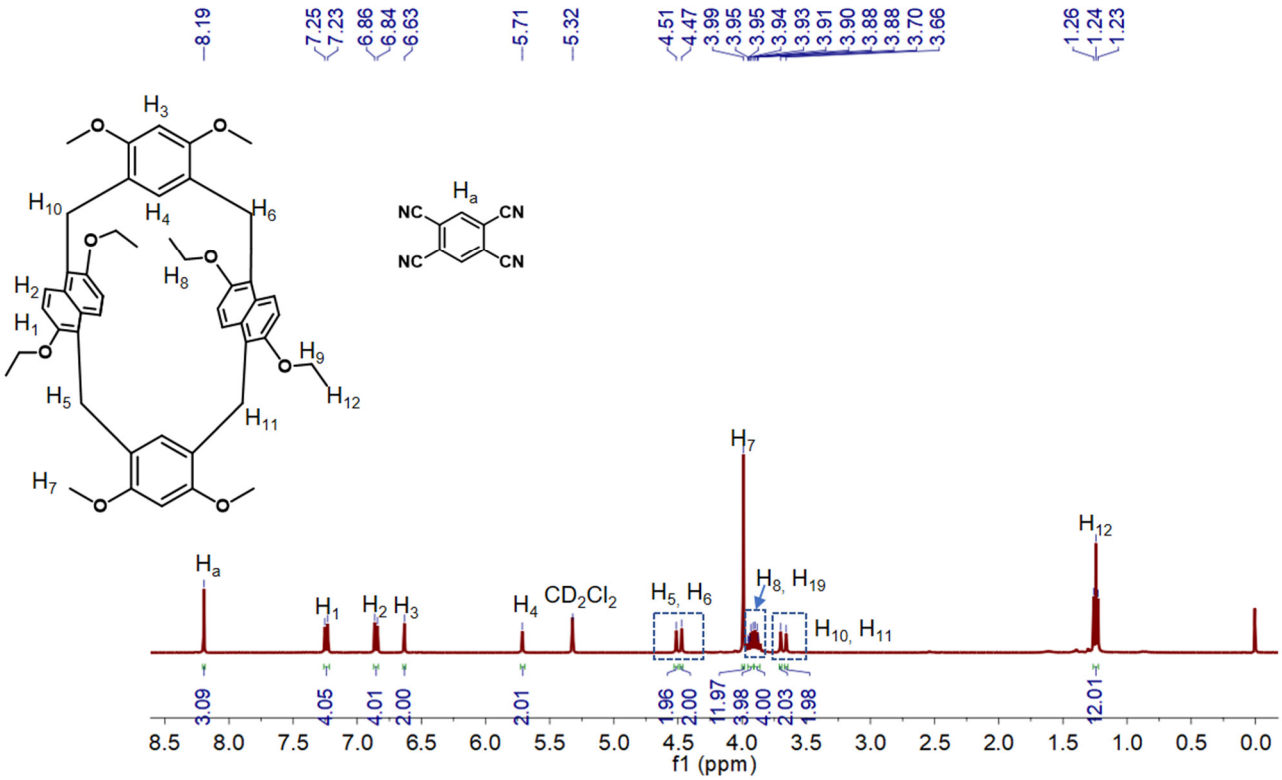


Supplementary Figure 23. Illustration of the (a) packing model of **H-TCNB**@CH_2Cl_2 and (b) C–H···N interactions between CH_2Cl_2 and **TCNB**. The **H** molecules are omitted for clarity. C–H···N distances: a = 2.342 Å, b = 3.218 Å.

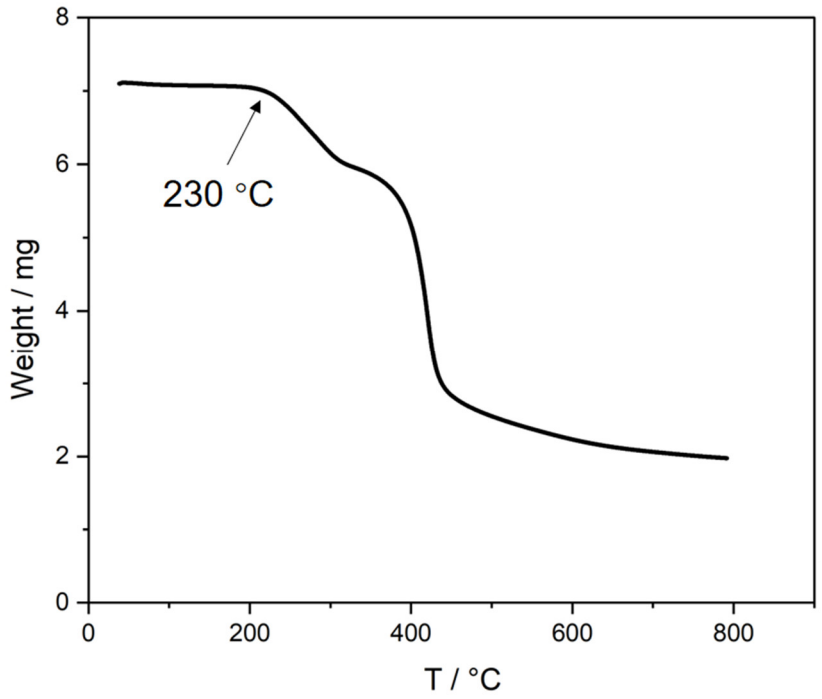


Supplementary Figure 24. The exo-wall π–π interaction between **H** and **TCNB** in the co-crystal structures of **H-TCNB**@CH_2Cl_2. The CH_2Cl_2 molecules are omitted for clarity. π–π distances: 3.372 Å and 3.267 Å.

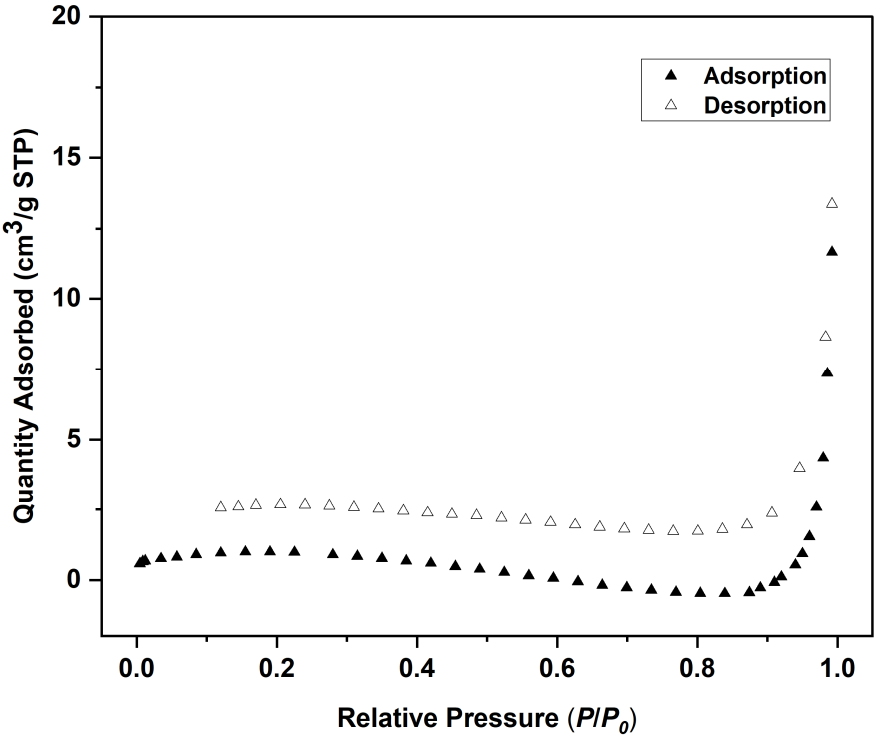
5. Characterization of H-TCNB*α*



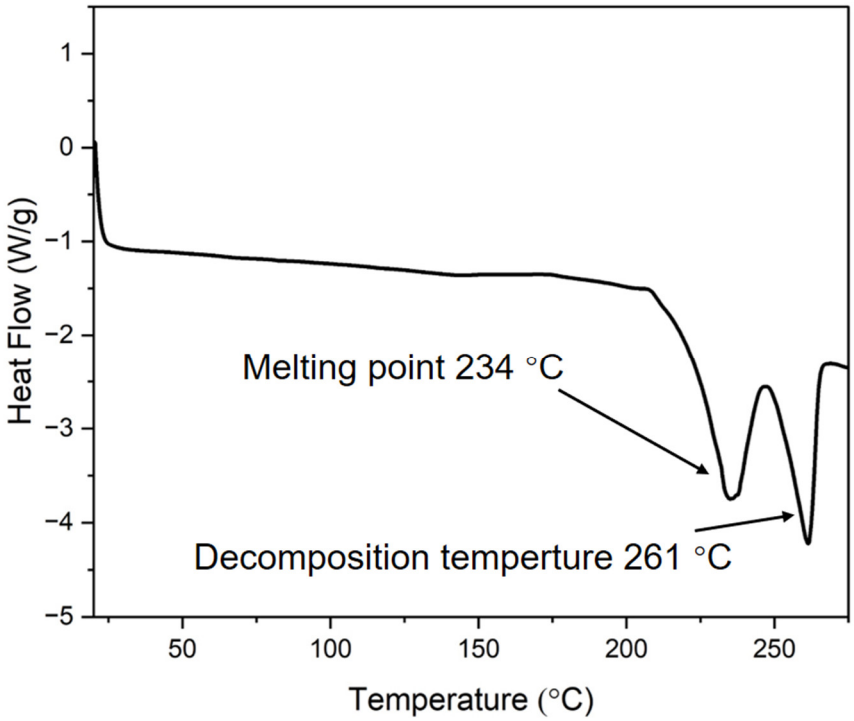
Supplementary Figure 25. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H-TCNB*α***.



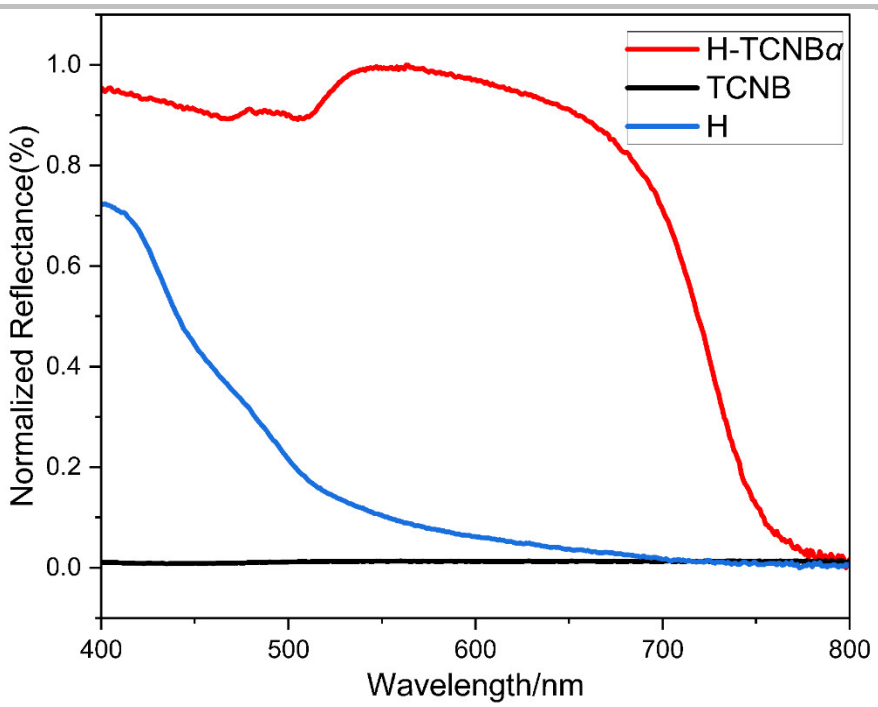
Supplementary Figure 26. Thermogravimetric analysis of **H-TCNB*α***.



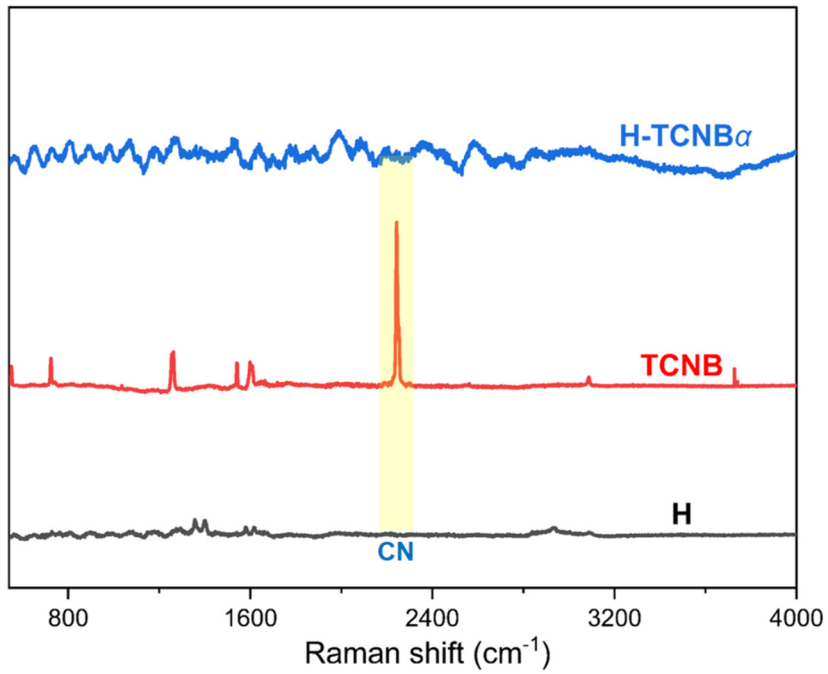
Supplementary Figure 27. N_2 adsorption-desorption isotherm of **H-TCNB*α***. The BET surface area value is 0.970 m^2/g. Adsorption, closed symbols; desorption, open symbols.



Supplementary Figure 28. DSC plot of **H-TCNB*α***.



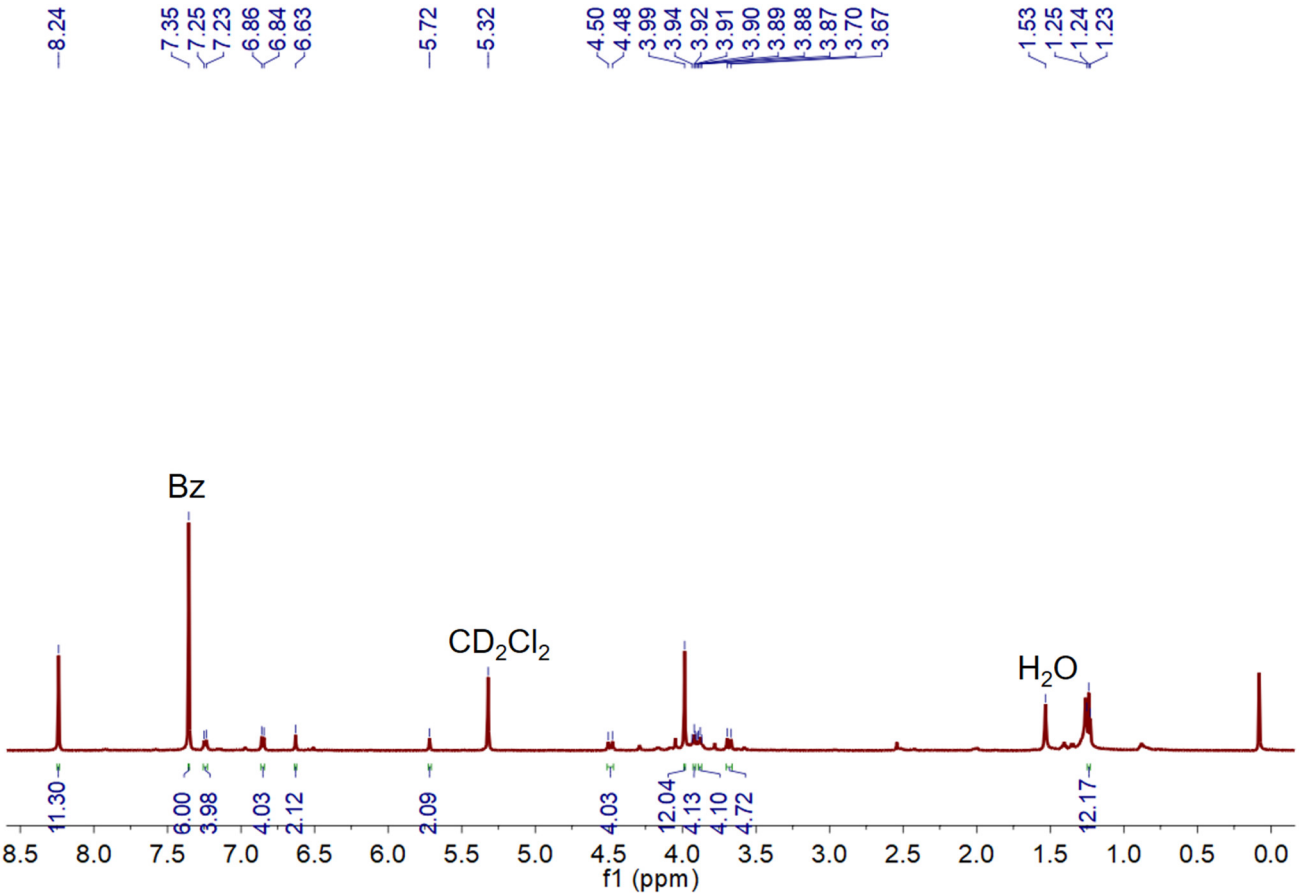
Supplementary Figure 29. Diffuse reflectance spectra of **H**, **TCNB** and **H-TCNB***α*.



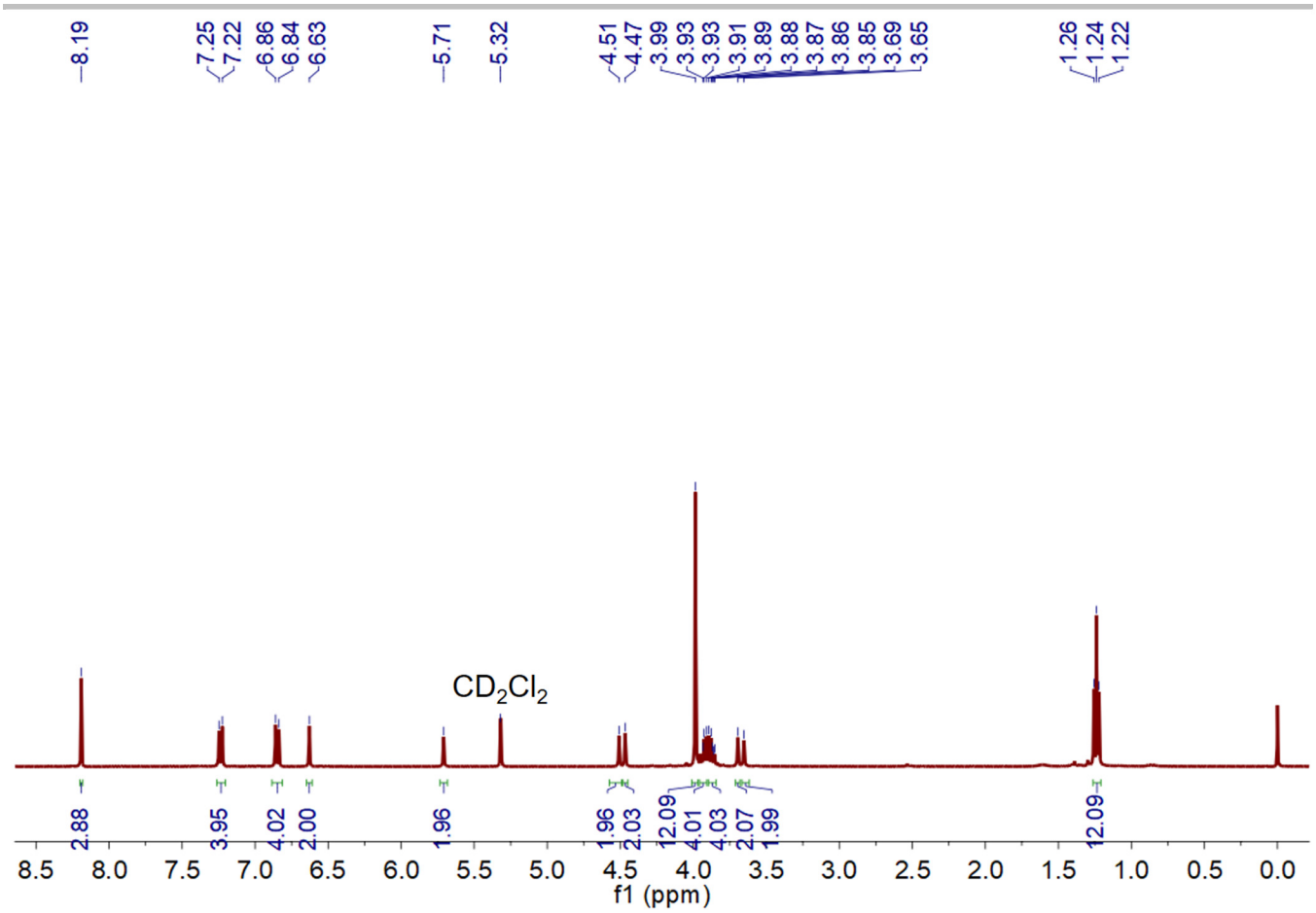
Supplementary Figure 30. Raman spectra of **H**, **TCNB**, **H-TCNB***α*.

6. Single-component adsorption experiments

^{1}H NMR experiments were performed by dissolving **H-TCNB*α*** after adsorption of single-component **Bz**/**Cy** vapor in CD_2Cl_2. TGA profiles were recorded using **H-TCNB*α*** after adsorption of single-component **Bz**/**Cy** vapor.[1]

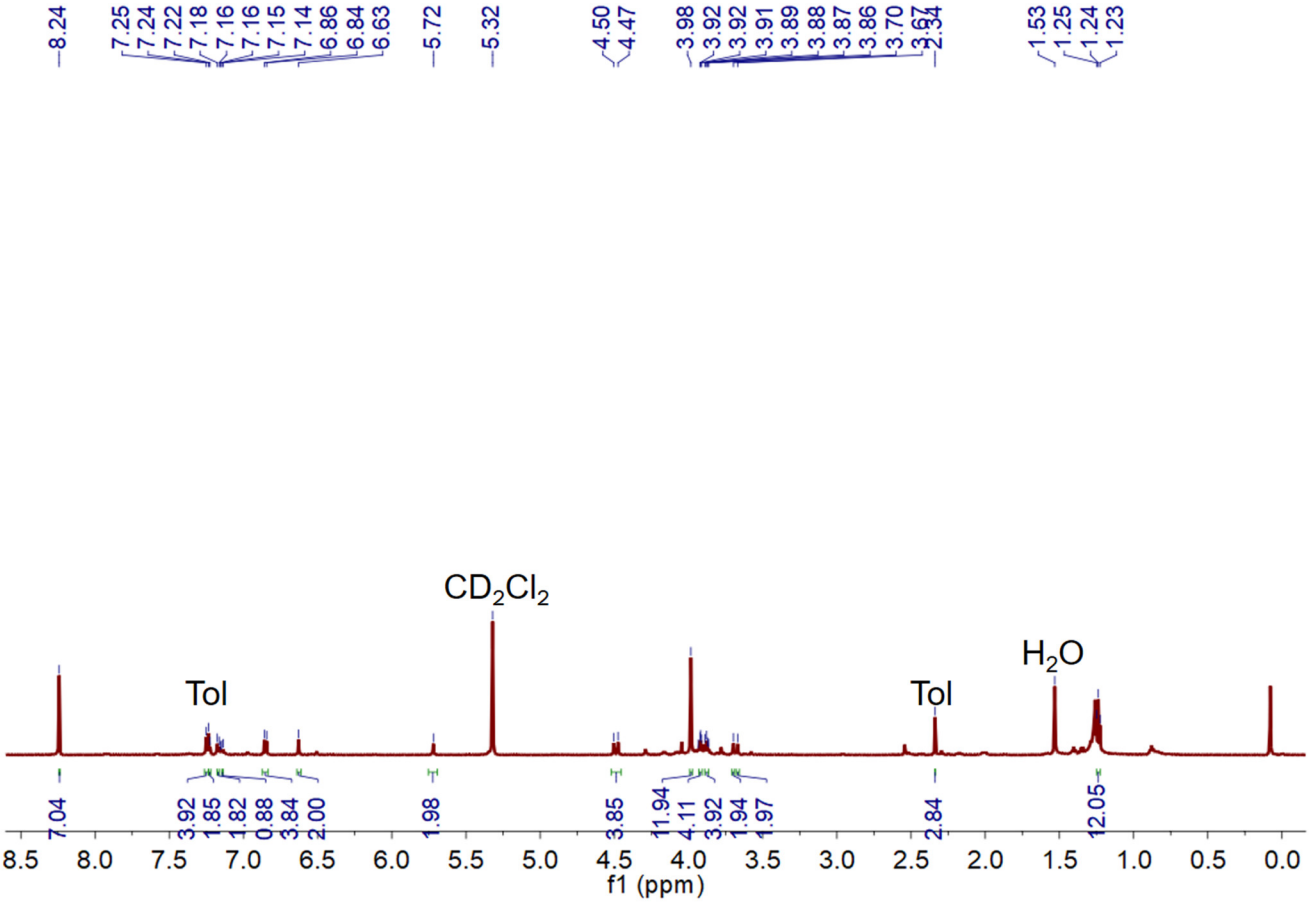


Supplementary Figure 31. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H-TCNB*α*** after sorption of **Bz** vapor for 24 h.

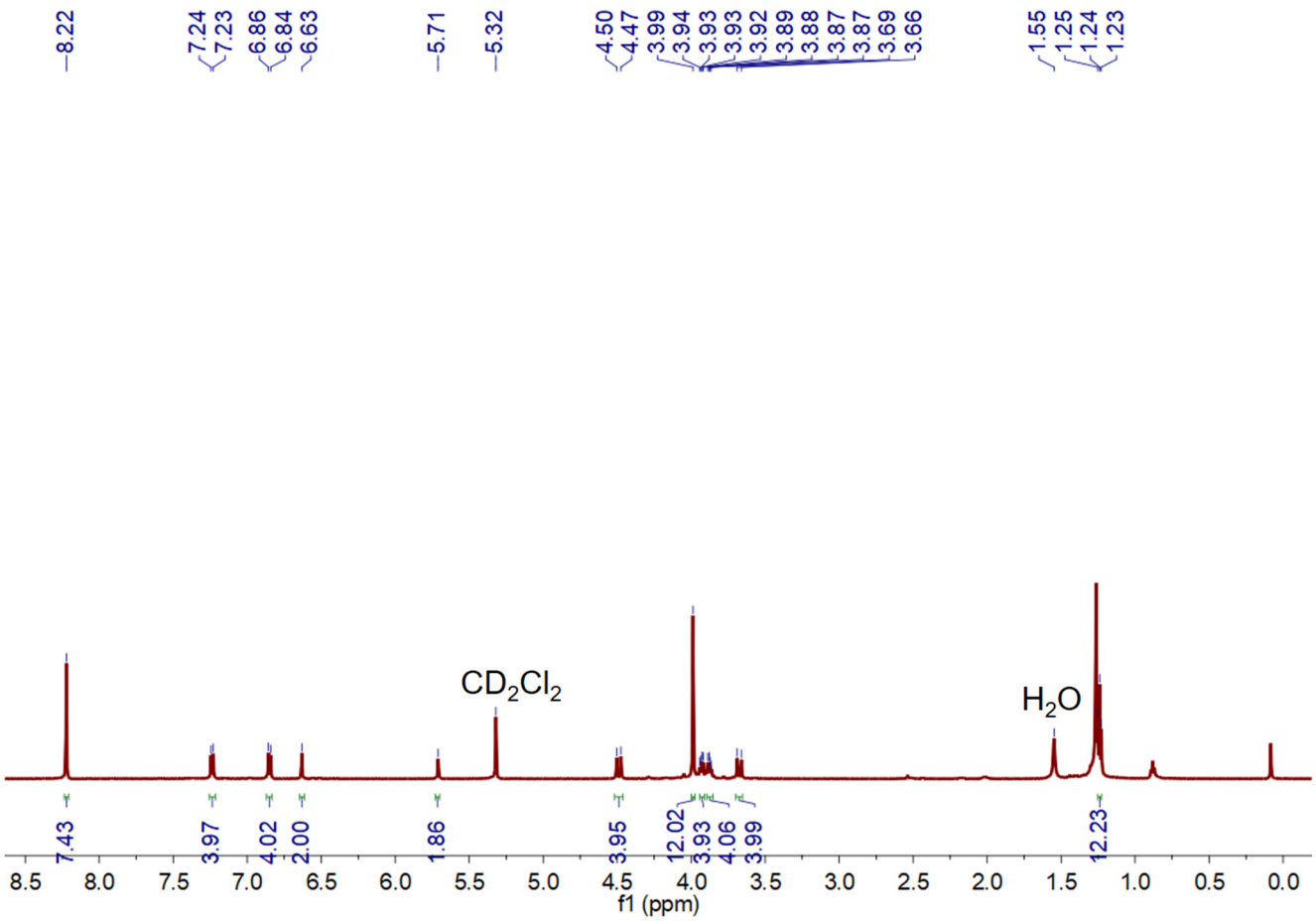


Supplementary Figure 32. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H-TCNB*α*** after sorption of **Cy** vapor for 24 h.

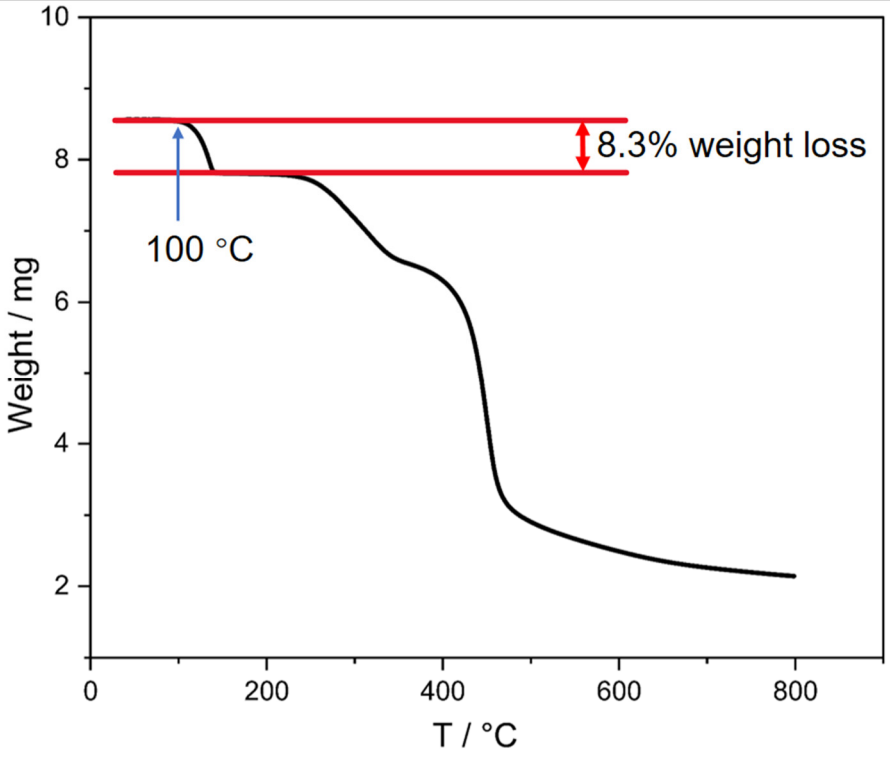
^{1}H NMR experiments were performed by dissolving **H-TCNB*α*** after adsorption of single-component **Tol**/**Py** vapor in CD_2Cl_2. TGA profiles were recorded using **H-TCNB*α*** after adsorption of single-component **Tol**/**Py** vapor.



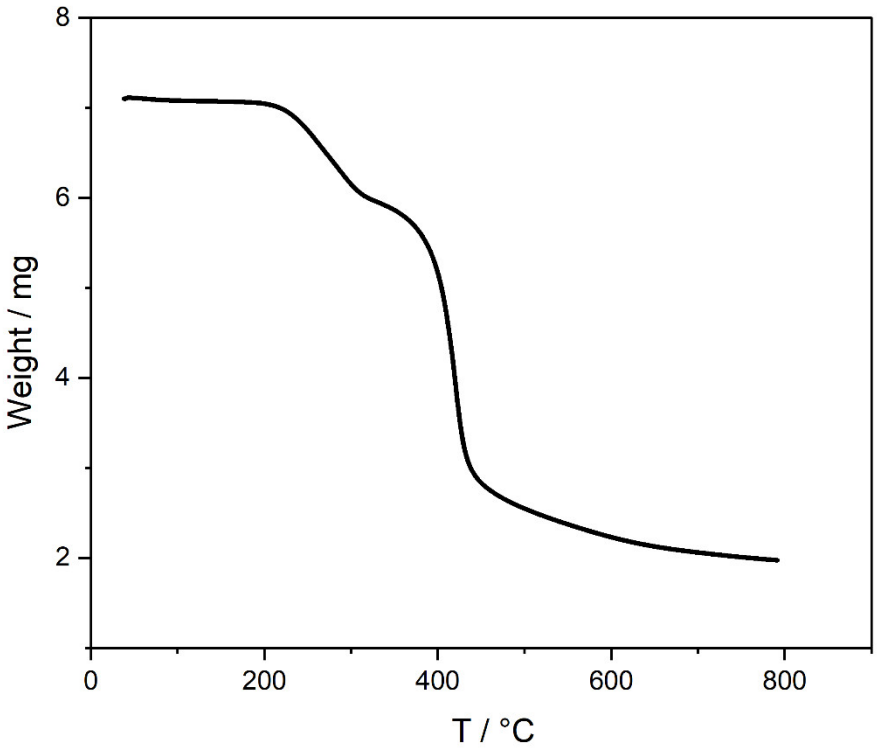
Supplementary Figure 33. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H-TCNB*α*** after sorption of **Tol** vapor for 24 h.



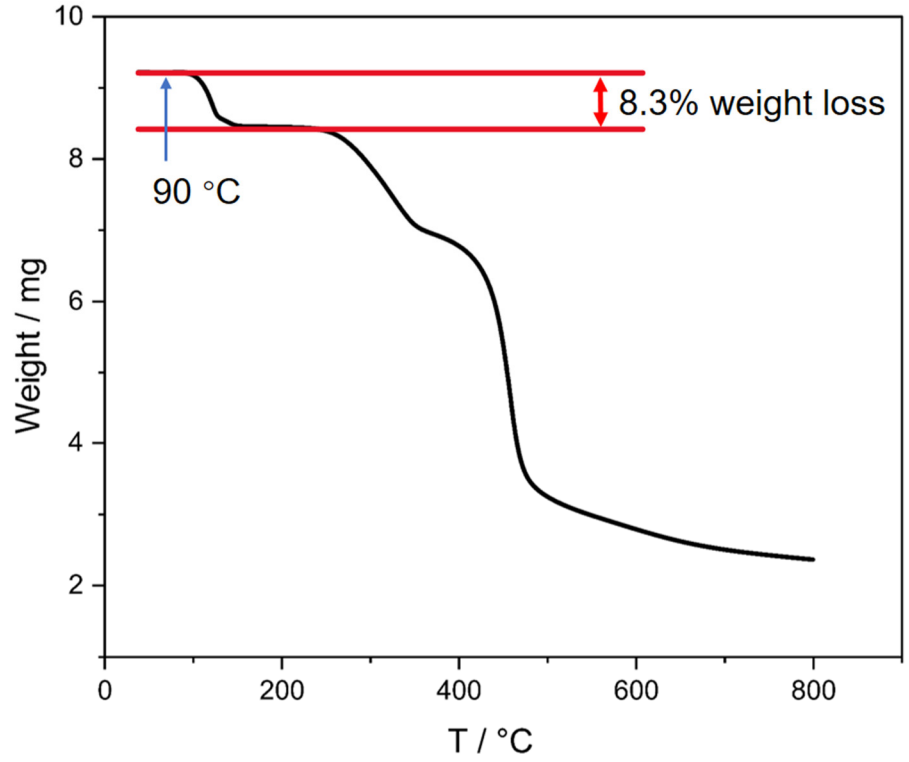
Supplementary Figure 34. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H-TCNB*α*** after sorption of **Py** vapor for 24 h.



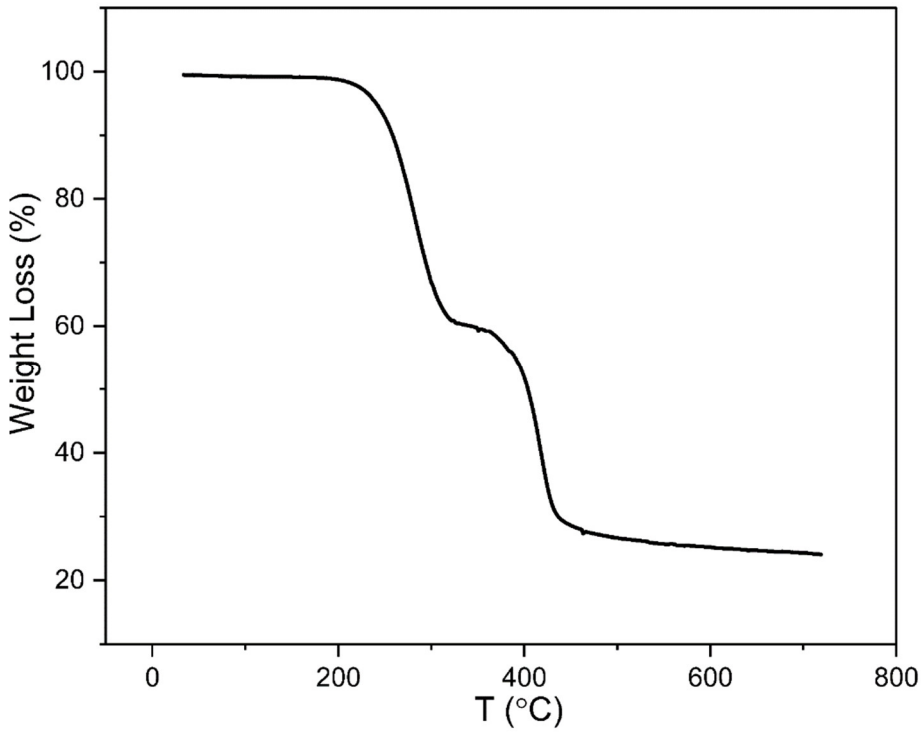
Supplementary Figure 35. Thermogravimetric analysis of **H-TCNB***α* after sorption of **Bz** vapor for 24 h. The weight loss below 200 °C can be calculated as one **Bz** molecule per **H-TCNB** molecule.



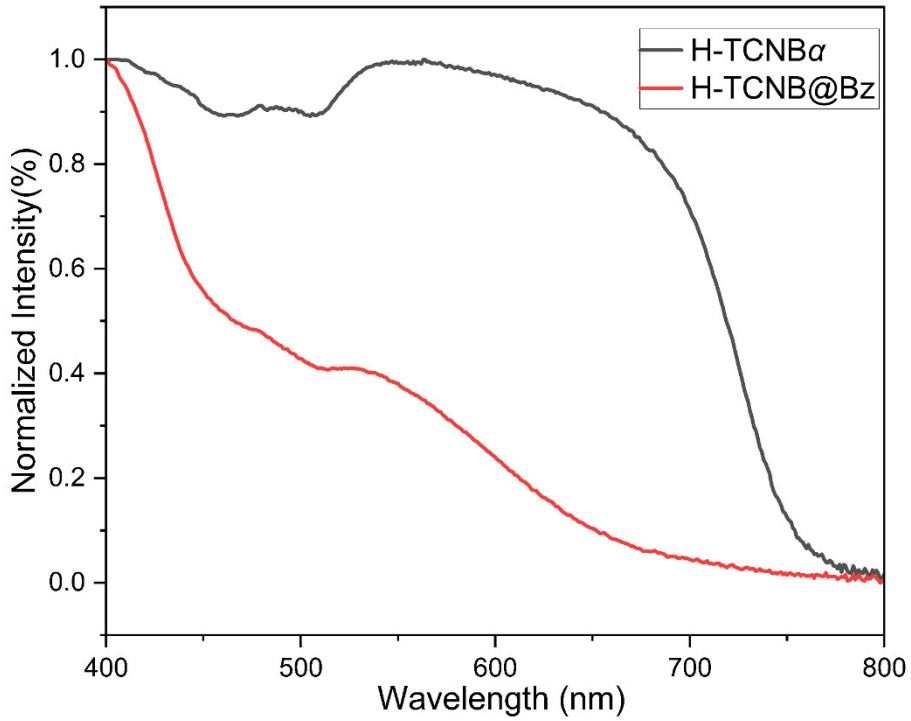
Supplementary Figure 36. Thermogravimetric analysis of **H-TCNB***α* after sorption of **Cy** vapor for 24 h.



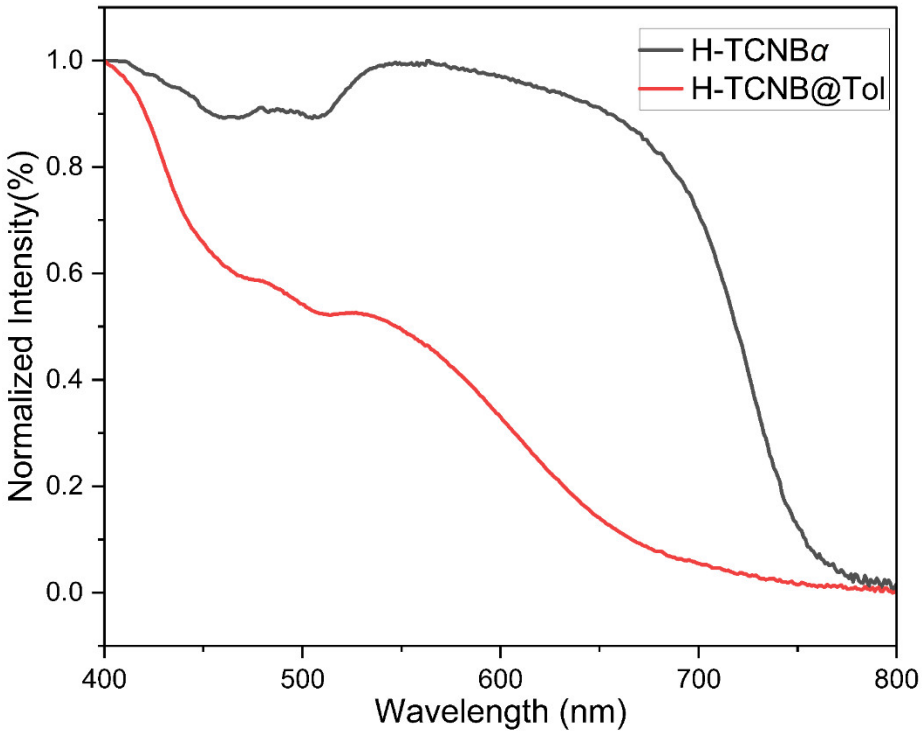
Supplementary Figure 37. Thermogravimetric analysis of **H-TCNB***α* after sorption of **Tol** vapor for 24 h. The weight loss below 150 °C can be calculated as 0.86 **Tol** molecule per **H-TCNB** molecule.



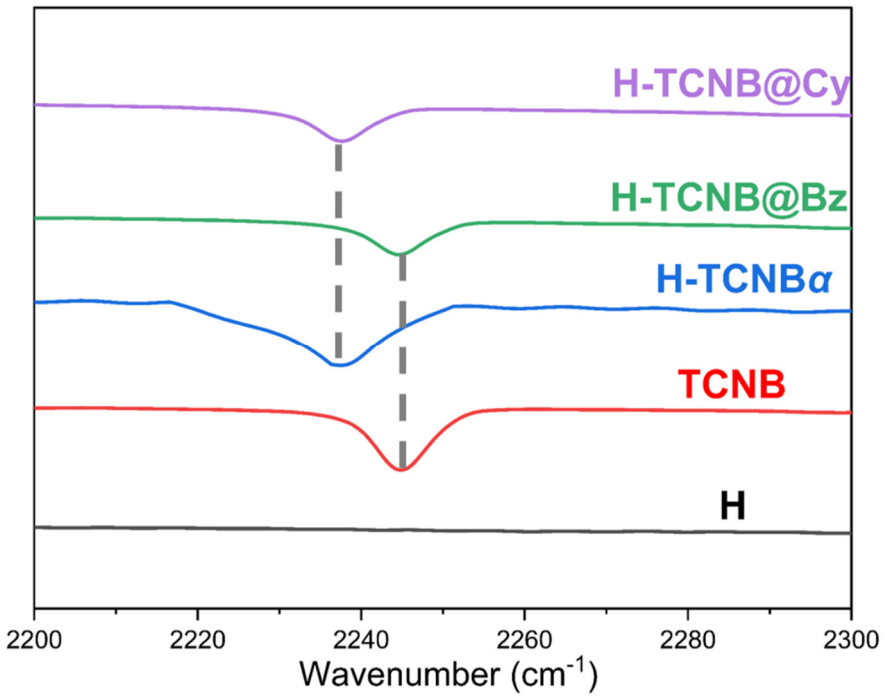
Supplementary Figure 38. Thermogravimetric analysis of **H-TCNB***α* after sorption of **Py** vapor for 24 h.



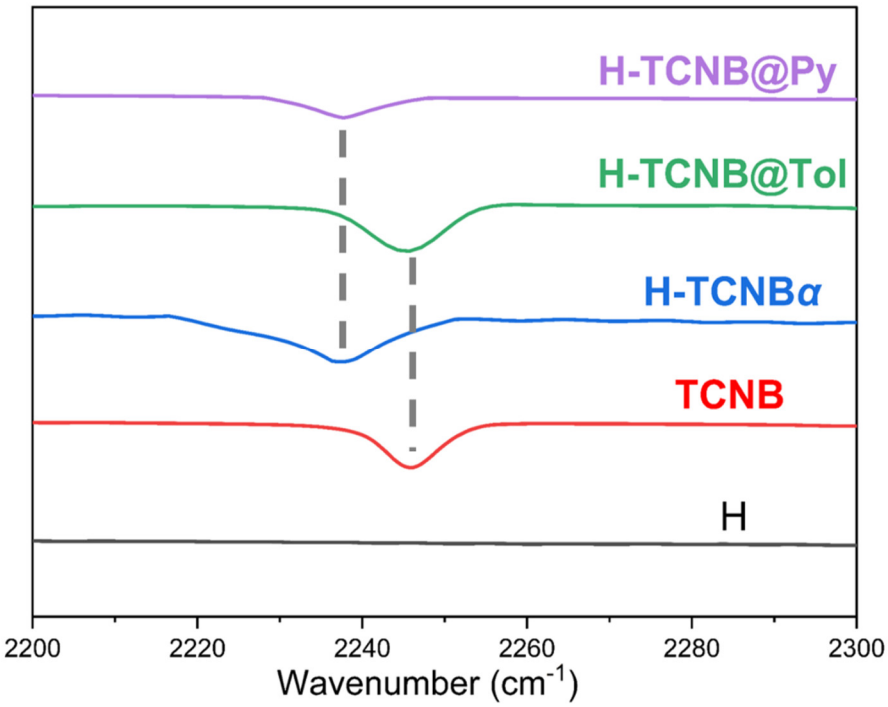
Supplementary Figure 39. Normalized diffuse reflectance spectra of **H-TCNB*α*** upon adsorption of **Bz**.



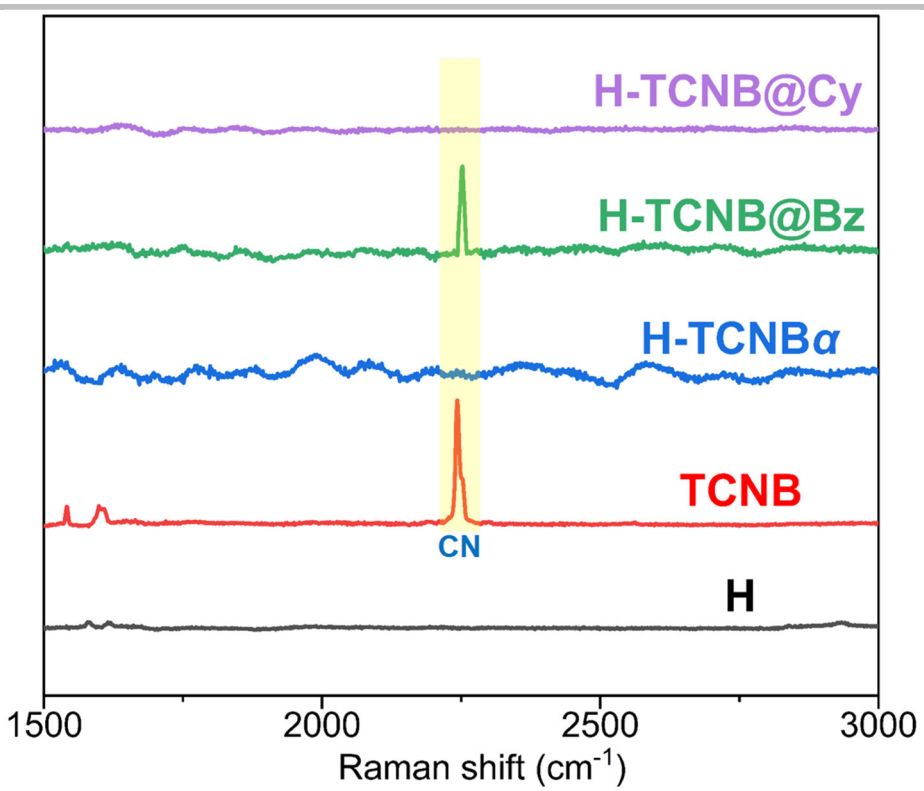
Supplementary Figure 40. Normalized diffuse reflectance spectra of **H-TCNB*α*** upon adsorption of **Tol**.



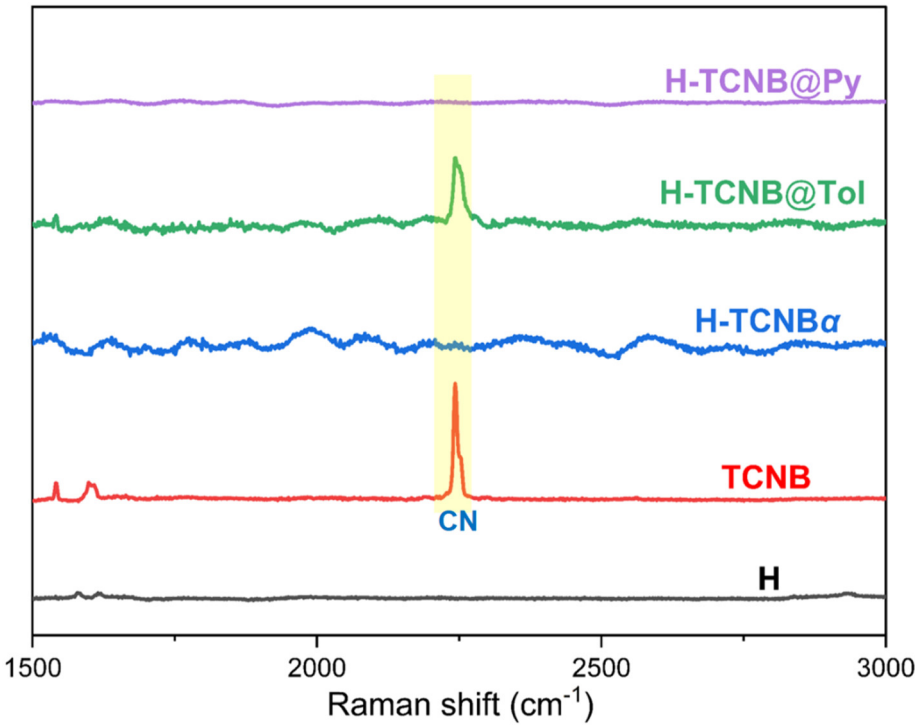
Supplementary Figure 41. Partial FT-IR spectra of **H**, **TCNB**, **H-TCNBα**, **H-TCNB@Bz** and **H-TCNB@Cy**.



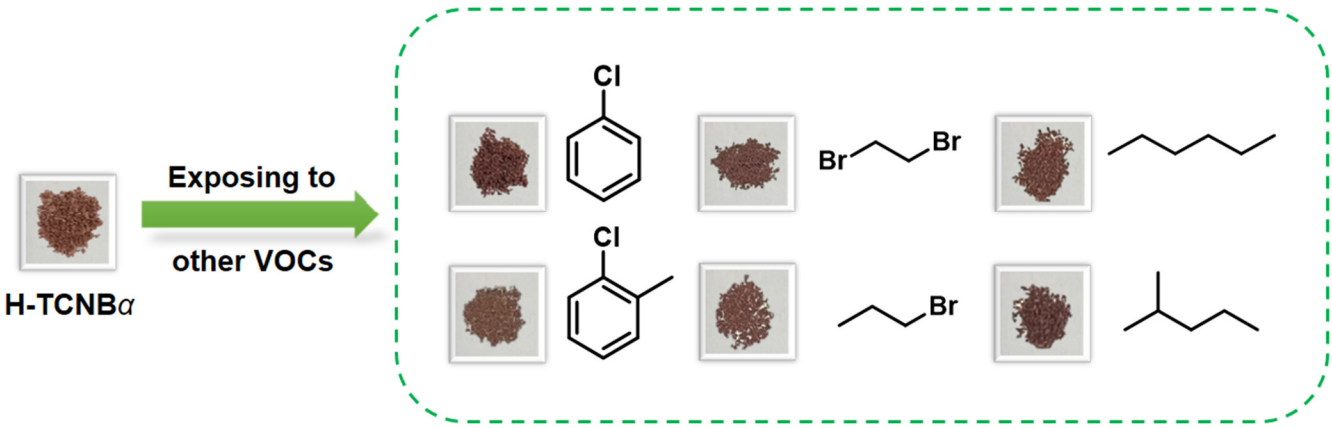
Supplementary Figure 42. Partial FT-IR spectra of **H**, **TCNB**, **H-TCNBα**, **H-TCNB@Tol** and **H-TCNB@Py**.



Supplementary Figure 43. Enlarged Raman spectra of **H**, **TCNB**, **H-TCNB*α***, **H-TCNB@Bz** and **H-TCNB@Cy**.

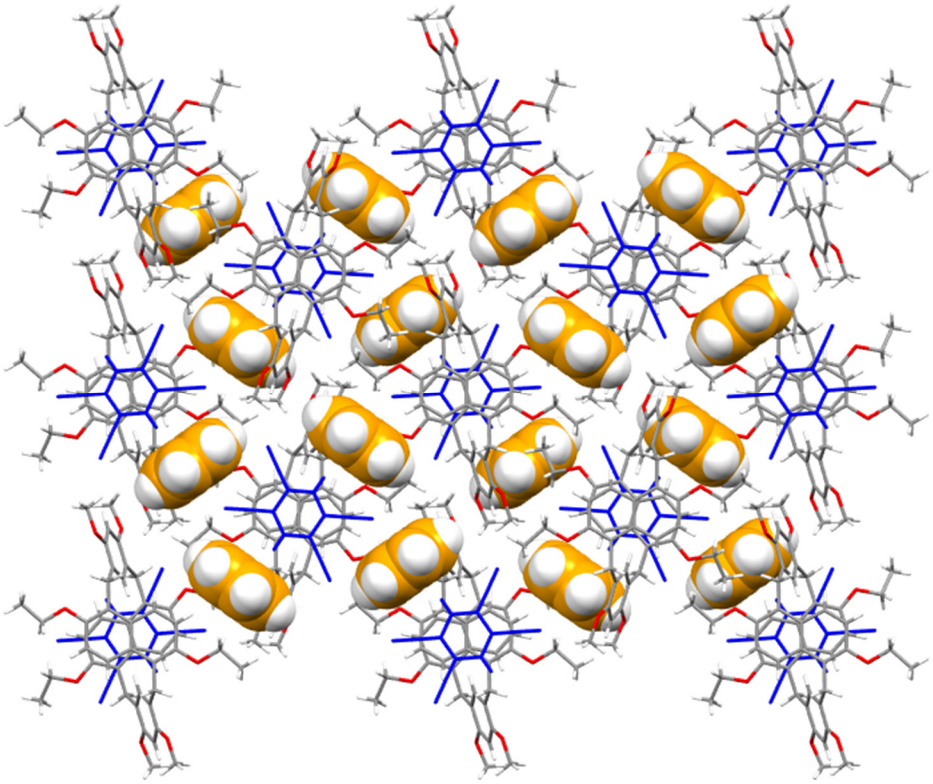


Supplementary Figure 44. Enlarged Raman spectra of **H**, **TCNB**, **H-TCNB*α***, **H-TCNB@Tol** and **H-TCNB@Py**.

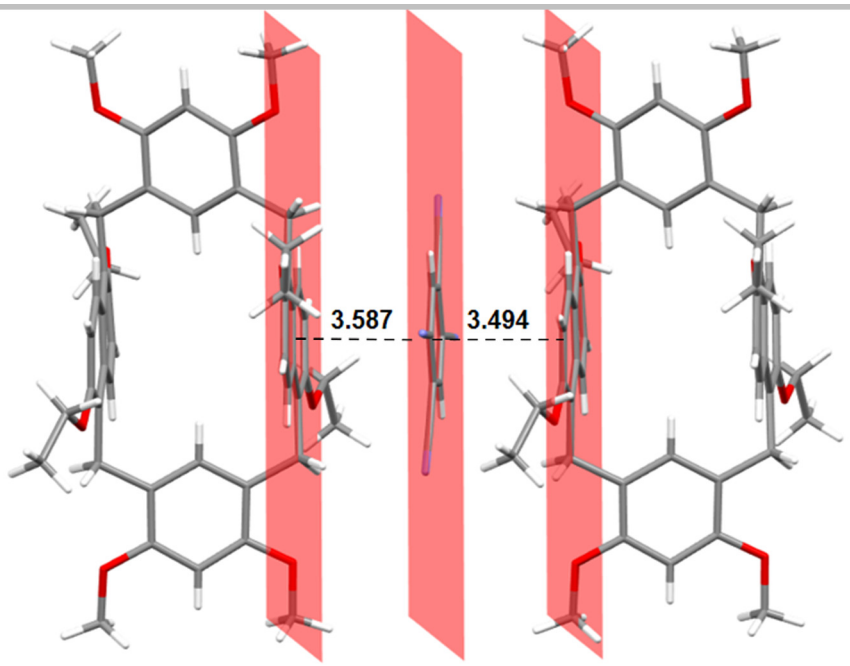


Supplementary Figure 45. The color of **H-TCNB*α*** after exposure to other VOCs.

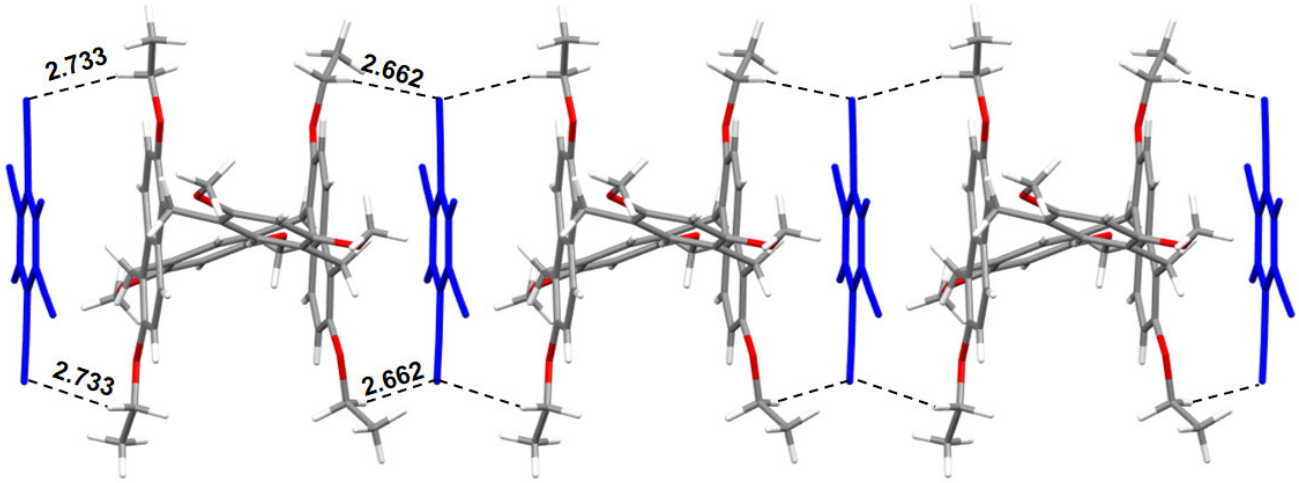
7. Non-covalent interaction analysis in single crystal structure of H-TCNB@Bz



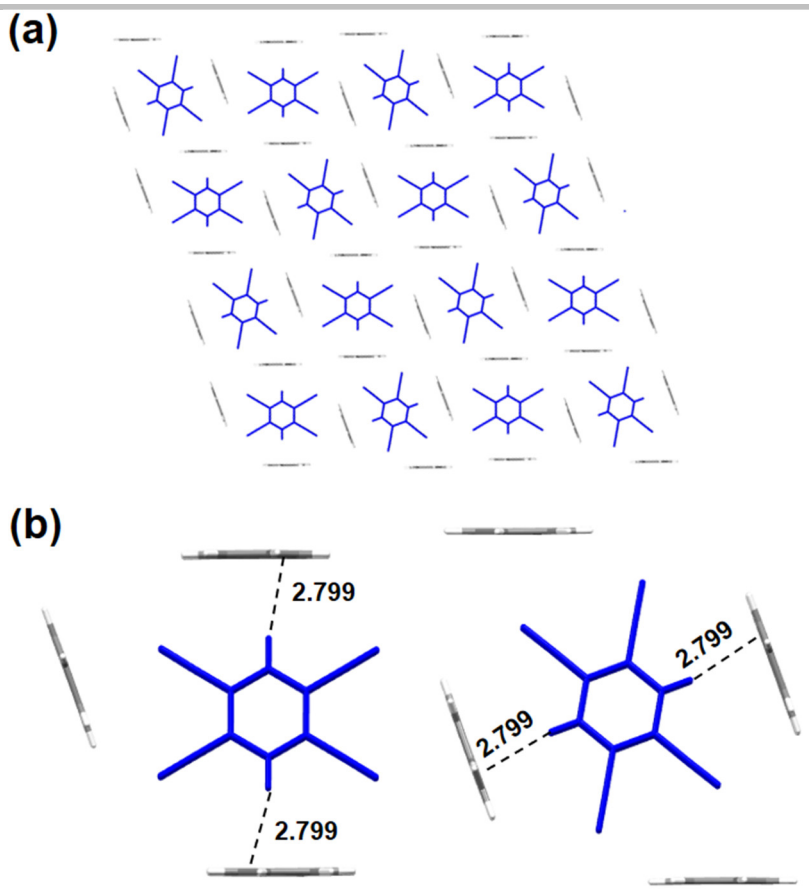
Supplementary Figure 46. Illustration of the packing model of **H-TCNB@Bz**.



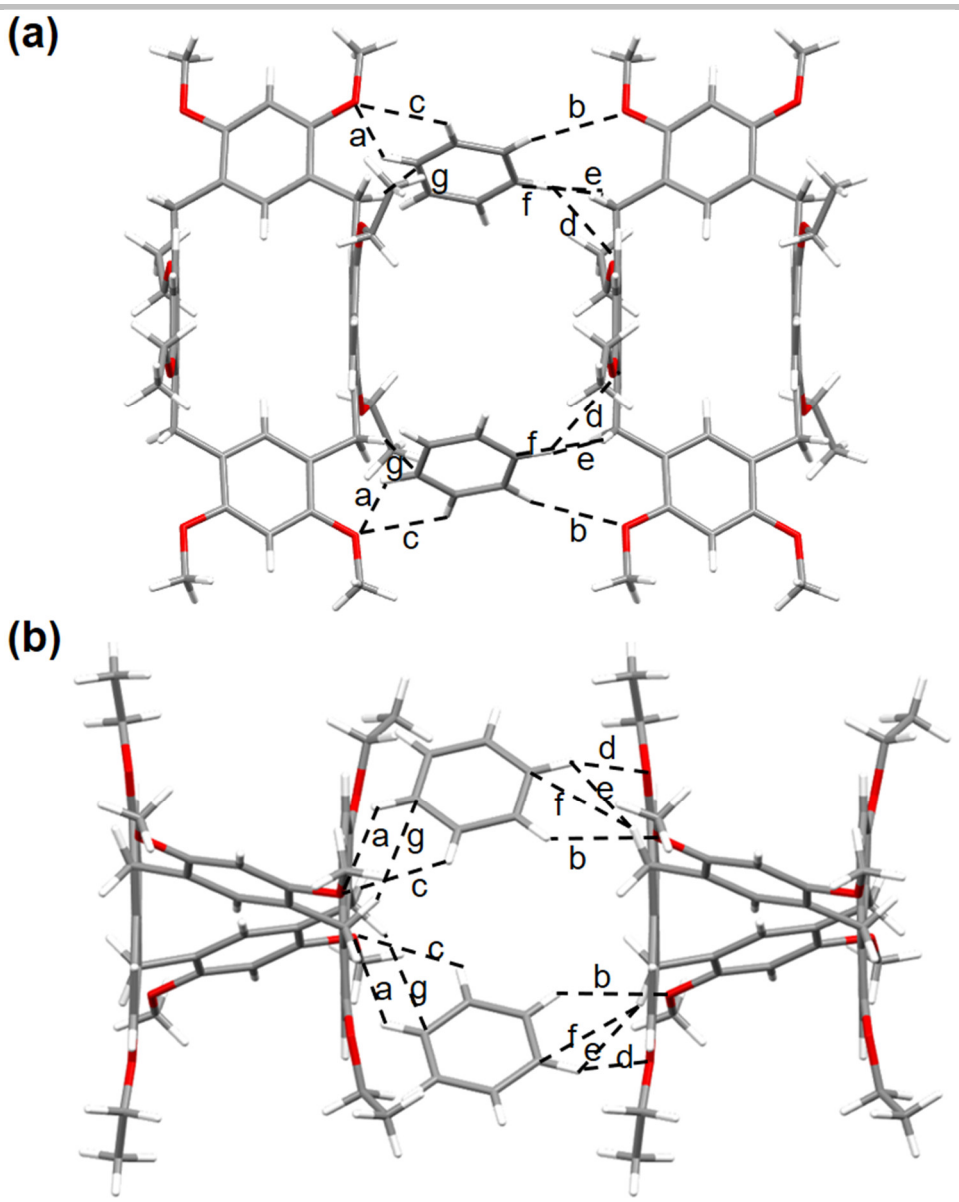
Supplementary Figure 47. The exo-wall π–π interactions between **H** and **TCNB** in **H-TCNB@Bz**. The **Bz** molecules are omitted for clarity. π–π distances: 3.587 Å and 3.494 Å.



Supplementary Figure 48. The exo-wall C–H···N interaction between **H** and **TCNB** in **H-TCNB@Bz**. The **Bz** molecules are omitted for clarity. C–H···N distances: 2.733 Å and 2.662 Å.



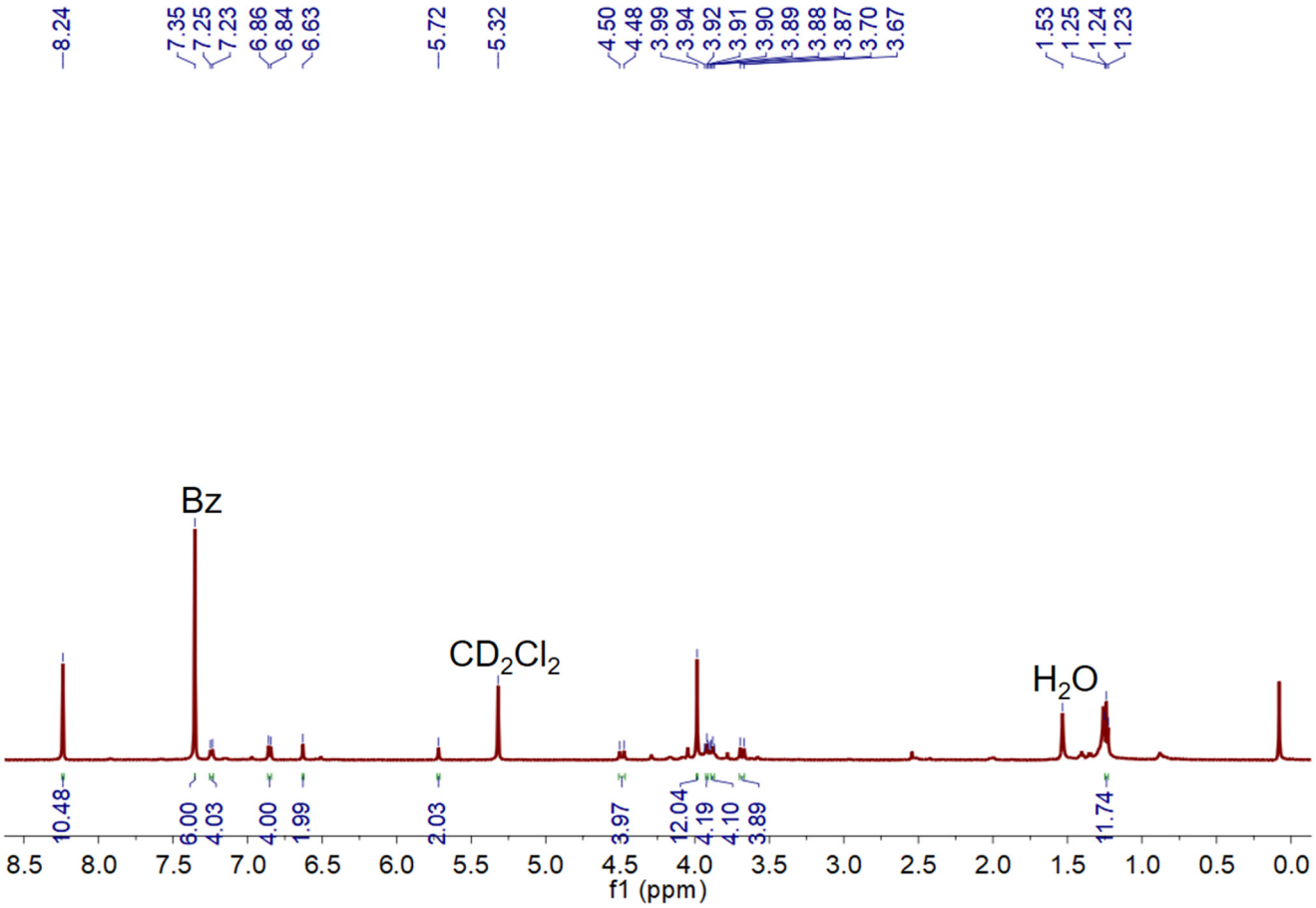
Supplementary Figure 49. Illustration of the (a) packing model of **H-TCNB@Bz** and (b) C–H···π interaction between **Bz** and **TCNB**. The **H** molecules are omitted for clarity. C–H···π distance: 2.799 Å.



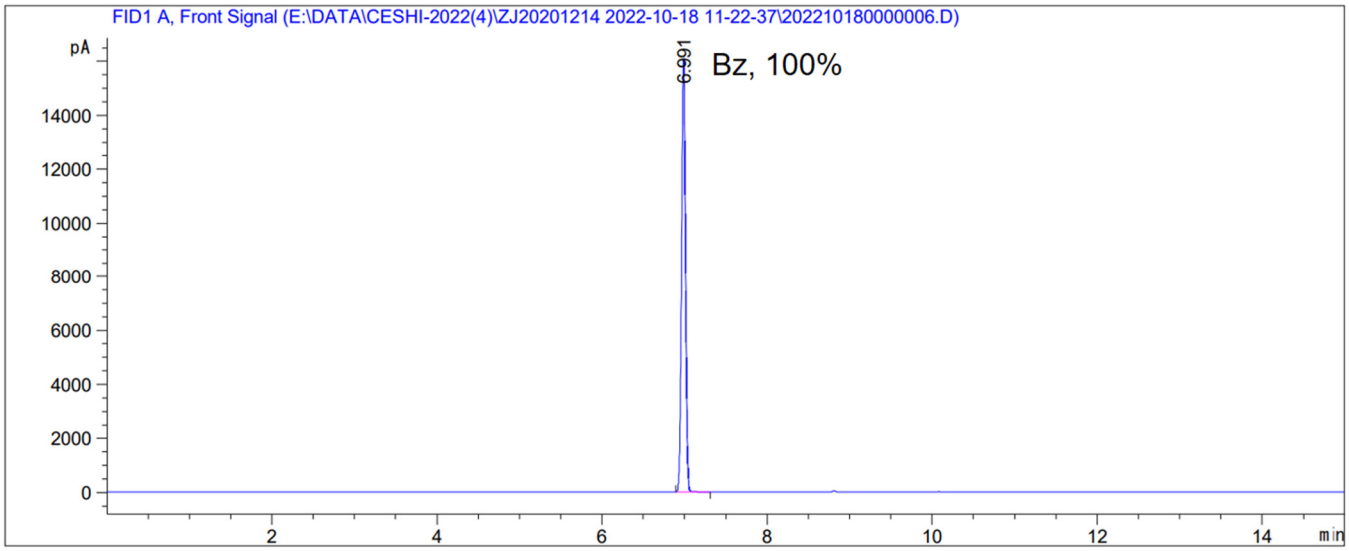
Supplementary Figure 50. Illustration of C–H···O and C–H···π interactions between **Bz** and **H**. The **TCNB** molecules are omitted for clarity. C–H···O distances: a = 2.707 Å, b = 2.685 Å, c = 2.669 Å. C–H···π distances: d = 2.685 Å, e = 2.234 Å, f = 2.800 Å, g = 2.804 Å.

8. Selectivity experiments of H-TCNB*α* for the mixture vapors of Bz and Cy.

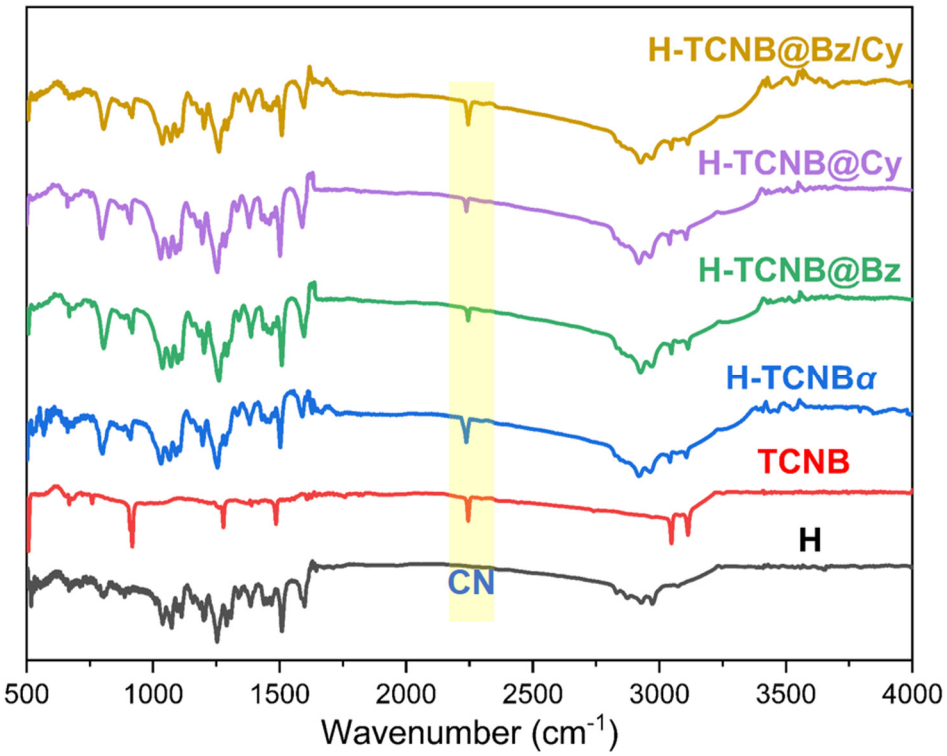
An open 5 mL vial containing 2 mg of **H-TCNB*α*** adsorbent was placed in a sealed 20 mL vial containing 1 mL of a **Bz/Cy** mixture (*v:v* = 1:1). Uptake in **H-TCNB*α*** was measured hour by hour by completely dissolving the crystals and measuring the ratio of **Bz** or **Cy** to **H-TCNB** by ^{1}H NMR. The relative uptakes of **Bz** and **Cy** in **H*α*** were 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 headspace gas chromatography.



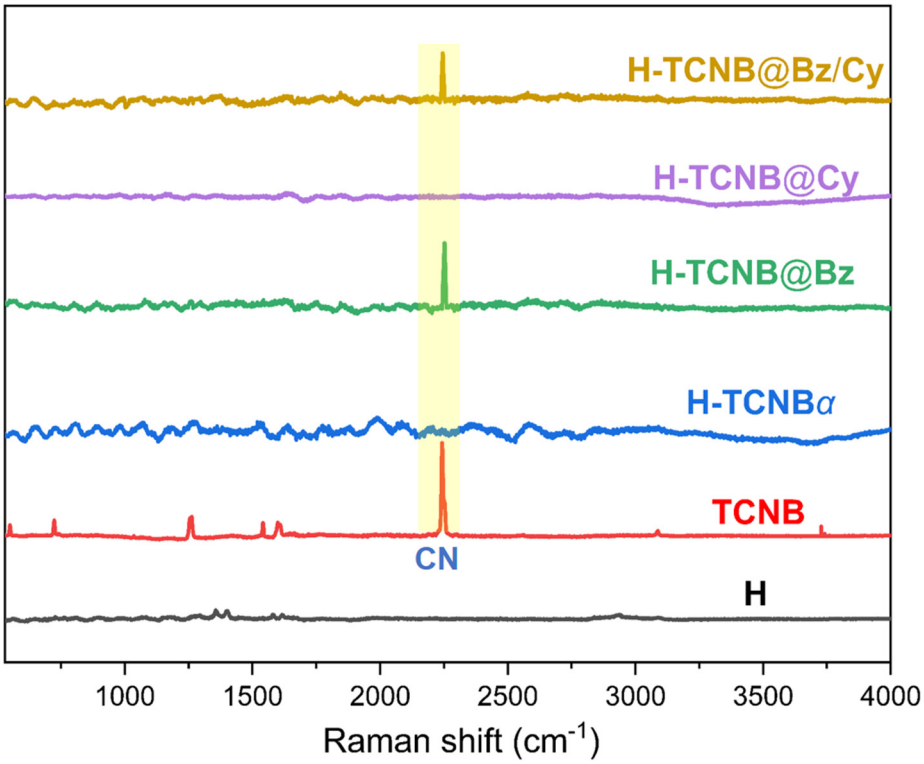
Supplementary Figure 51. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H-TCNB*α*** after sorption of a **Bz/Cy** mixture (*v:v* = 1:1) vapor for 12 h.



Supplementary Figure 52. Relative uptakes of **Bz** and **Cy** adsorbed in **H-TCNB*α*** for 24 h using head space gas chromatography.



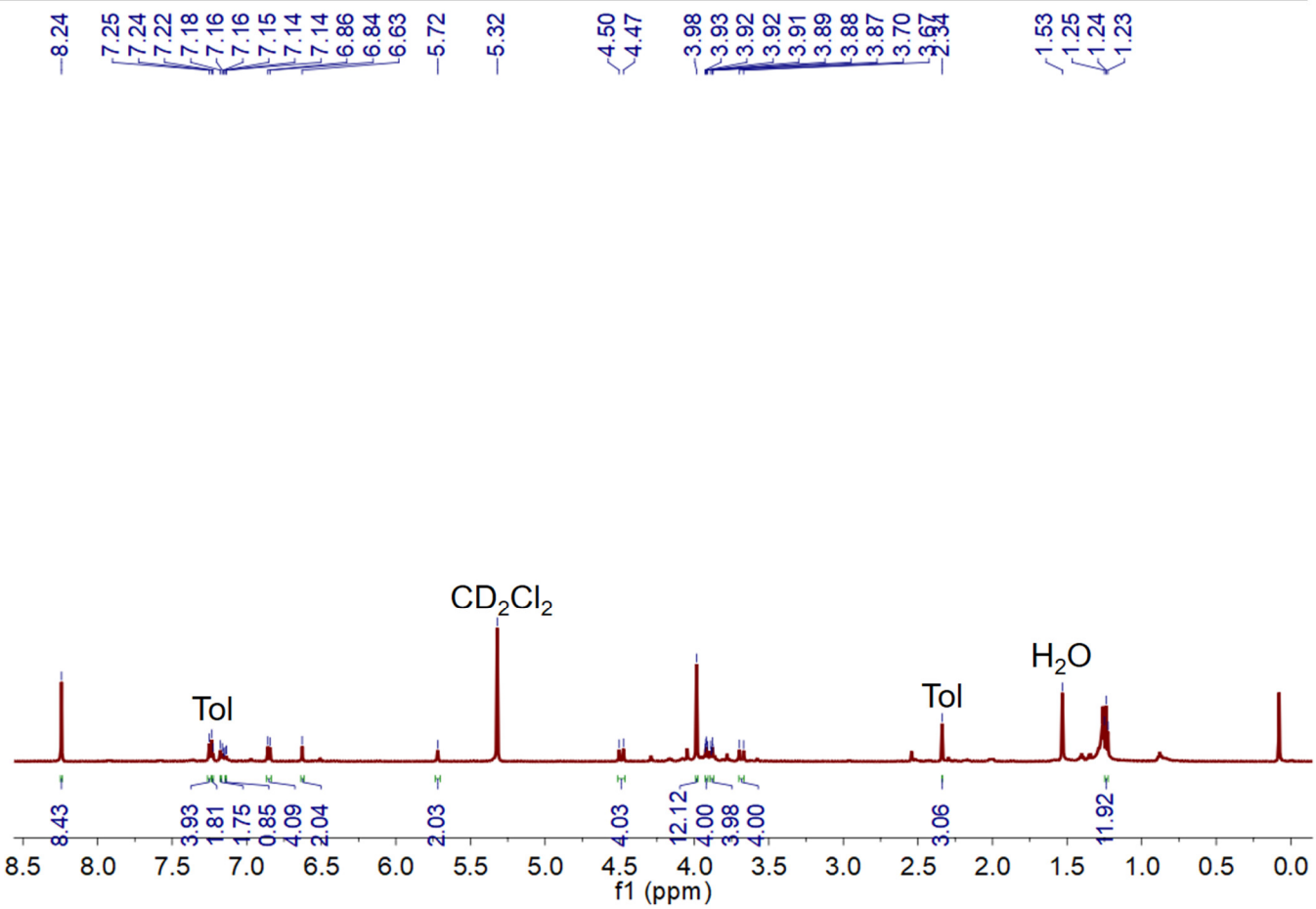
Supplementary Figure 53. FT-IR spectra of **H**, **TCNB**, **H-TCNB*α***, **H-TCNB@Bz**, **H-TCNB@Cy**, and **H-TCNB@Bz/Cy**.



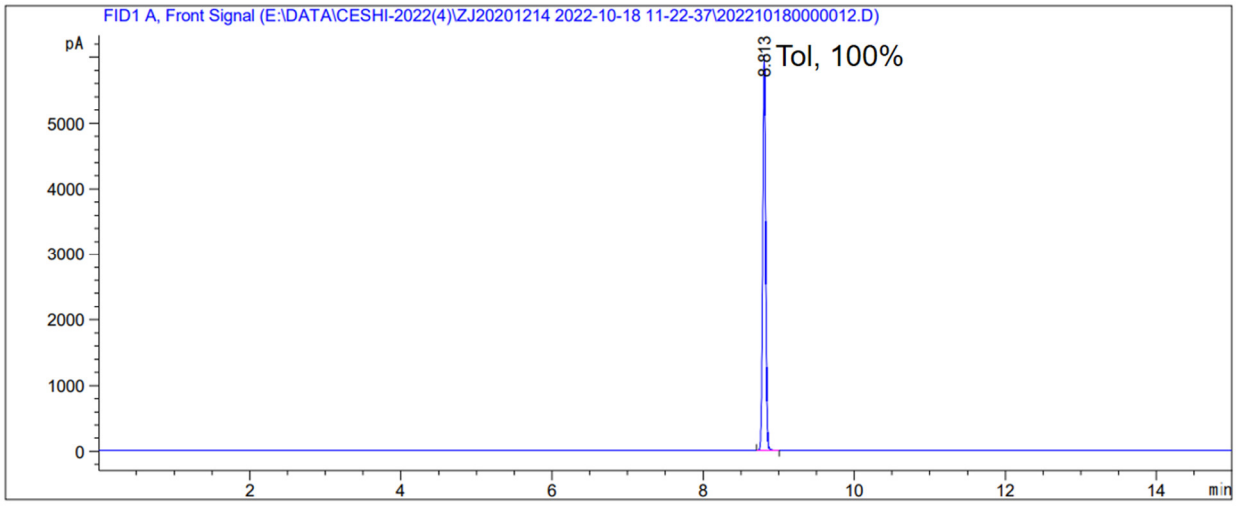
Supplementary Figure 54. Raman spectra of **H**, **TCNB**, **H-TCNB*α***, **H-TCNB@Bz**, **H-TCNB@Cy**, and **H-TCNB@Bz/Cy**.

9. Selectivity experiments of H-TCNB*α* for the mixture vapors of Tol and Py.

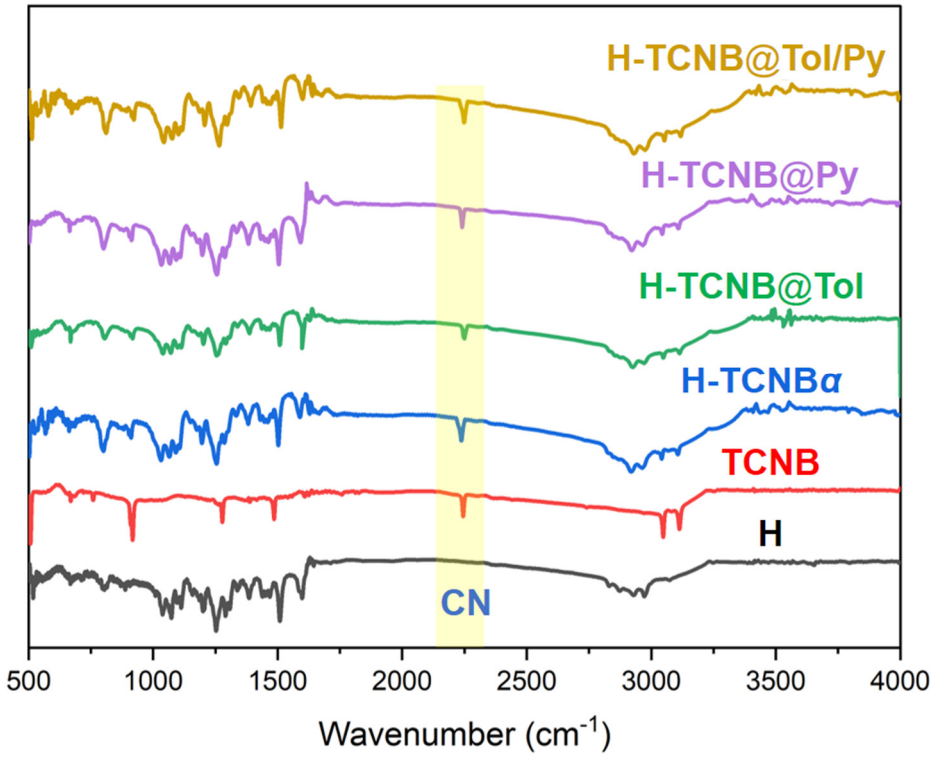
An open 5 mL vial containing 2 mg of **H-TCNB*α*** adsorbent was placed in a sealed 20 mL vial containing 1 mL of a **Tol/Py** mixture (*v:v* = 1:1). Uptake in **H-TCNB*α*** was measured hour by hour by completely dissolving the crystals and measuring the ratio of **Tol** or **Py** to **H-TCNB** by ^{1}H NMR. The relative uptakes of **Tol** and **Py** in **H*α*** were also measured by heating the crystals to release the adsorbed vapor and detecting the relative amounts of **Tol** and **Py** in the released vapor using headspace gas chromatography.



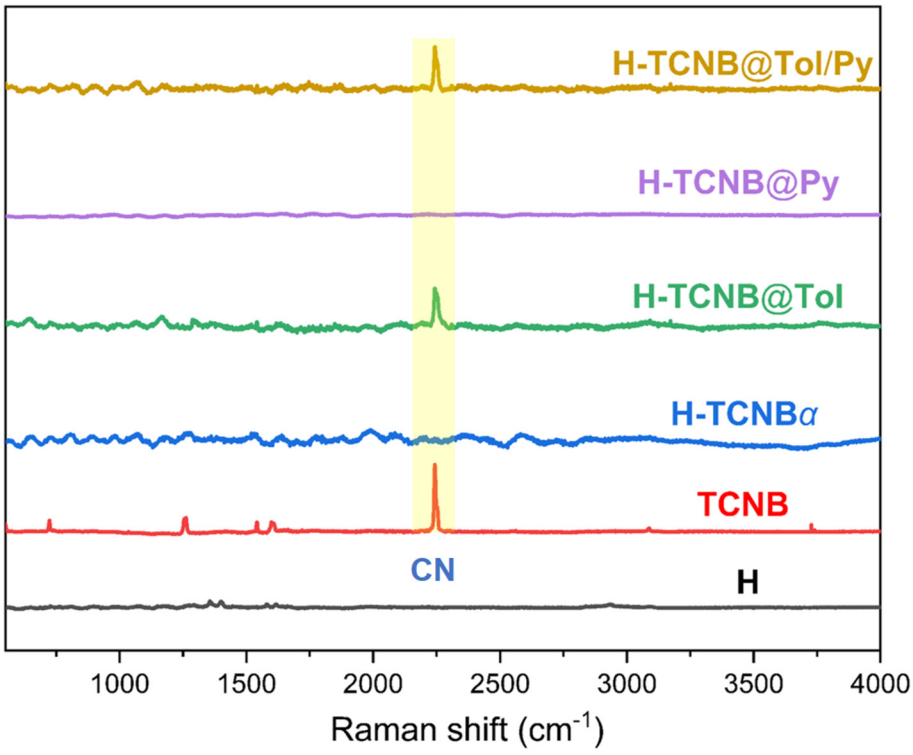
Supplementary Figure 55. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H*α*** after sorption of a **Tol/Py** mixture (*v:v* = 1:1) vapor for 24 h.



Supplementary Figure 56. Relative uptakes of **Tol** and **Py** adsorbed in **H-TCNB*α*** for 24 h using head space gas chromatography.

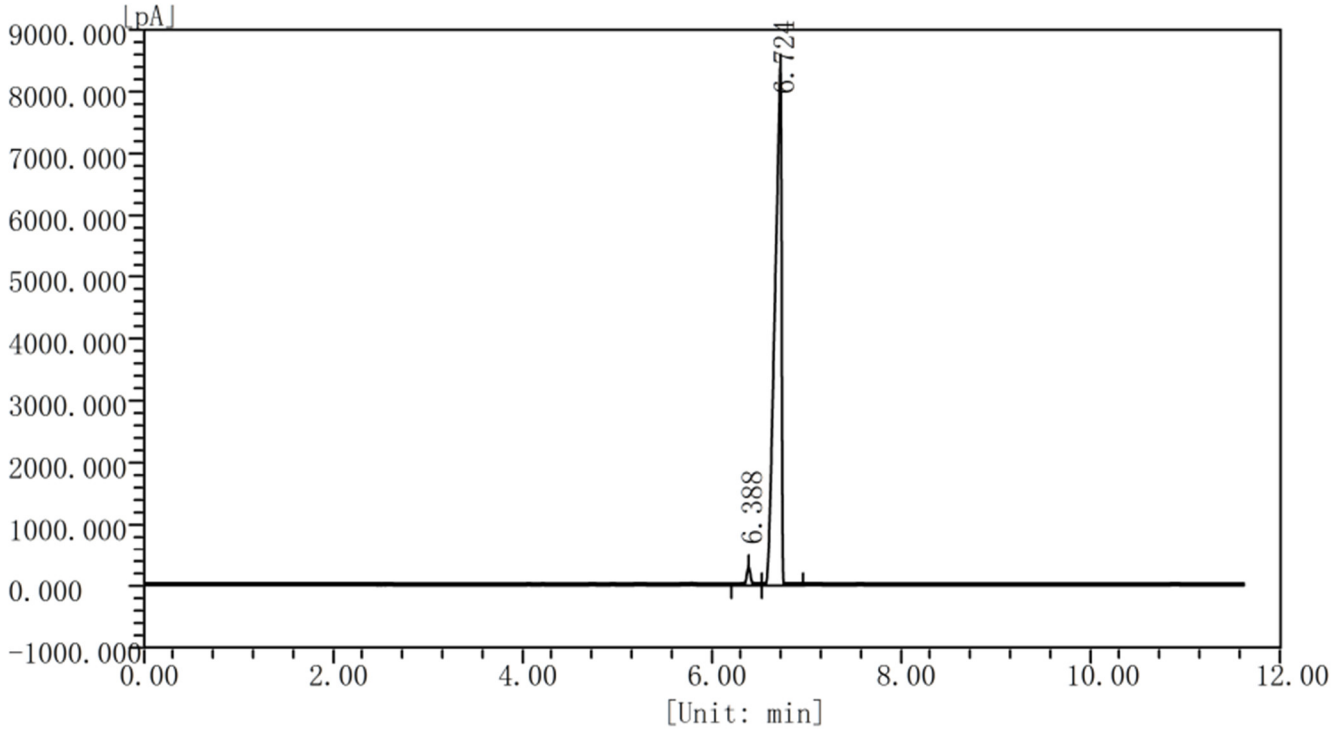


Supplementary Figure 57. FT-IR spectra of **H**, **TCNB**, **H-TCNBα**, **H-TCNB@Tol**, **H-TCNB@Py**, and **H-TCNB@Tol/Py**.



Supplementary Figure 58. Raman spectra of **H**, **TCNB**, **H-TCNBα**, **H-TCNB@Tol**, **H-TCNB@Py**, and **H-TCNB@Tol/Py**.

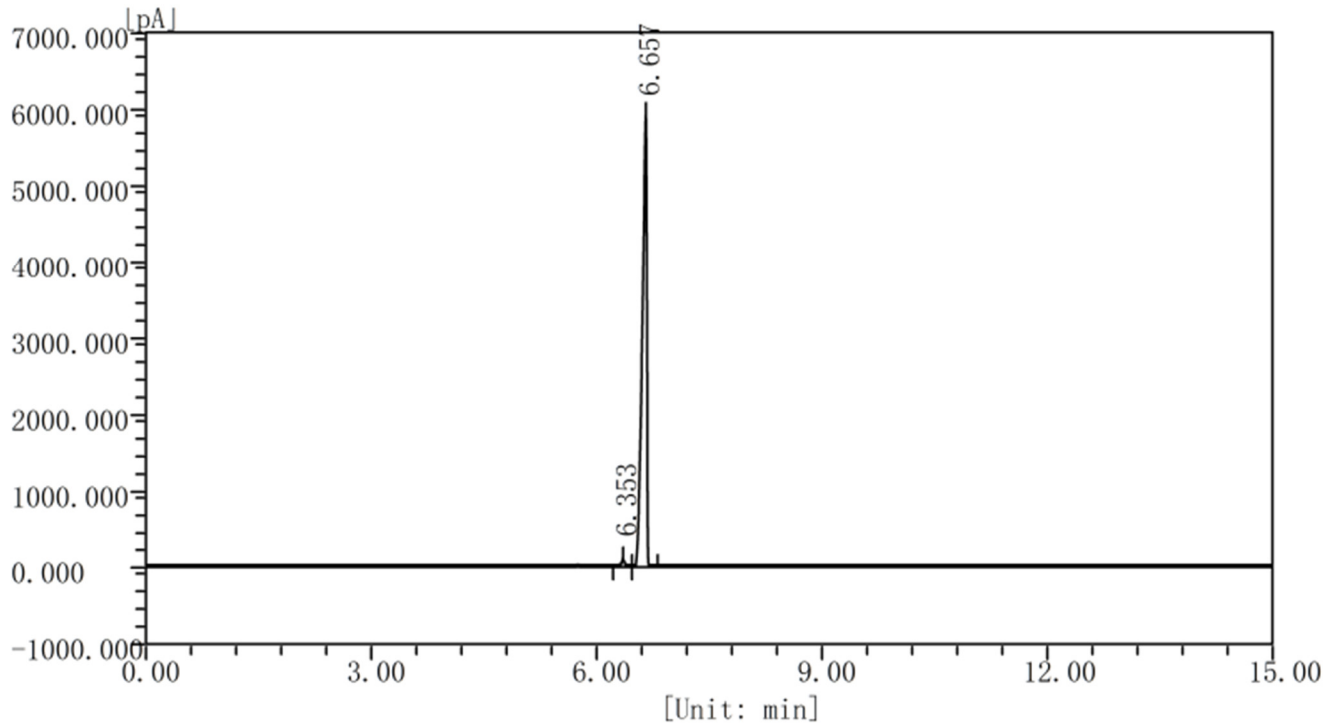
10. Purity experiments of liquid Cy or Py H-TCNB*α*



分析结果

峰序	组分名	保留时间 [min]	峰高 [uV]	峰面积 [uV*s]	峰面积 [%]	含量 [%]
1	苯	6.388	291542.0	824061.4	1.9910	1.9910
2	环己烷	6.724	8397338.9	40565863.0	98.0090	98.0090
		总计:	8688881.0	41389924.0	100.0000	100.0000

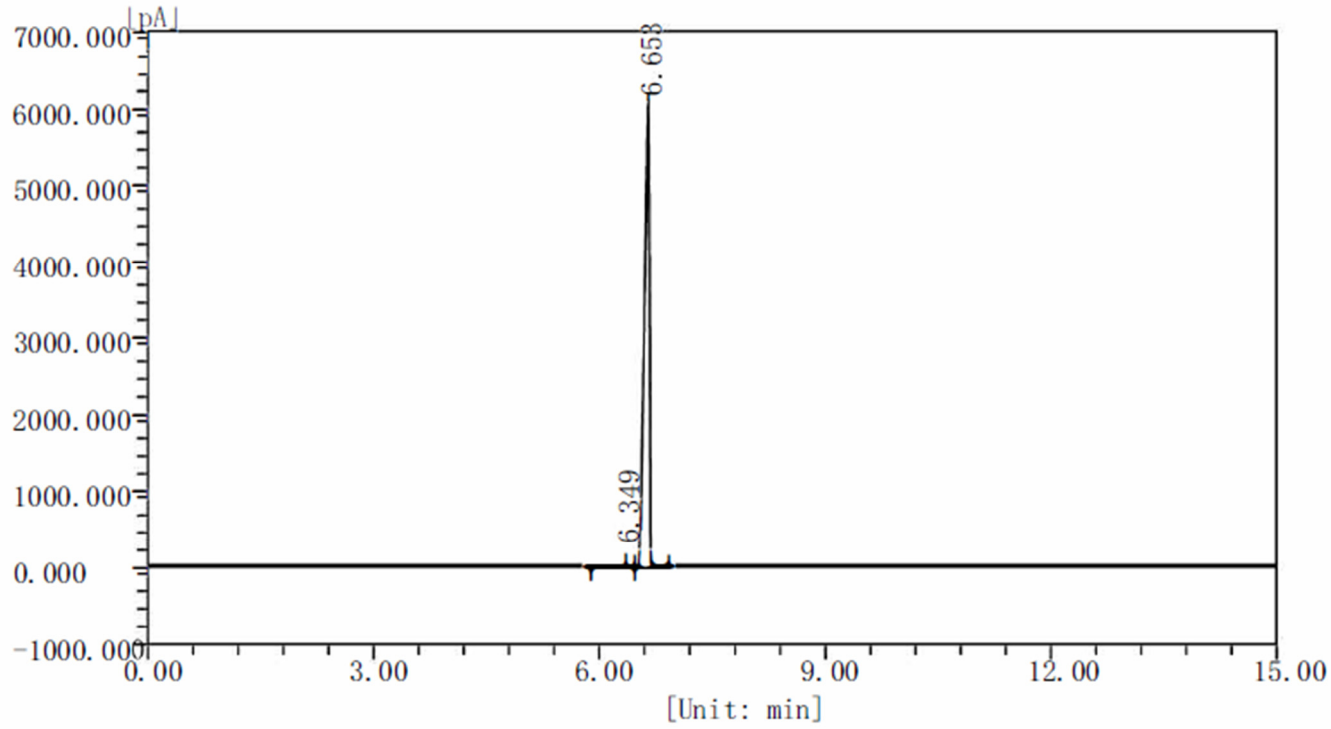
Supplementary Figure 59. GC analysis of the sample of 98:2 **Cy**/**Bz**.



分析结果

峰序	组分名	保留时间 [min]	峰高 [uV]	峰面积 [uV*s]	峰面积 [%]	含量 [%]
1	苯	6.353	99565.2	301520.9	1.2052	1.2052
2	环己烷	6.657	5925516.1	24715940.6	98.7948	98.7948
		总计:	6025081.0	25017462.0	100.0000	100.0000

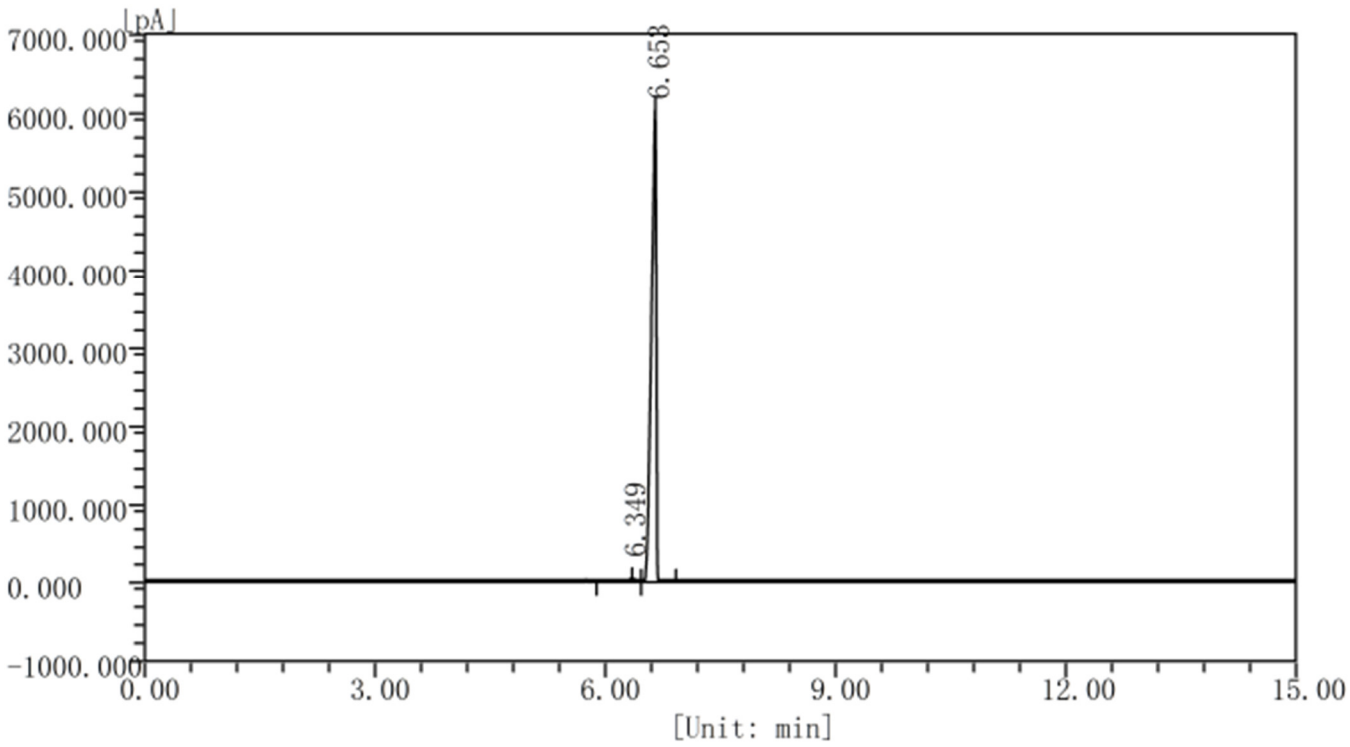
Supplementary Figure 60. GC analysis of the 98:2 **Cy**/**Bz** after adsorption by **H-TCNB*α*** (3.00 mg).



分析结果

峰序	组分名	保留时间 [min]	峰高 [uV]	峰面积 [uV*s]	峰面积 [%]	含量 [%]
1	苯	6.349	63596.9	222584.7	0.5680	0.5680
2	环己烷	6.653	8940172.8	38964739.9	99.4320	99.4320
		总计:	9003769.7	39187324.6	100.0000	100.0000

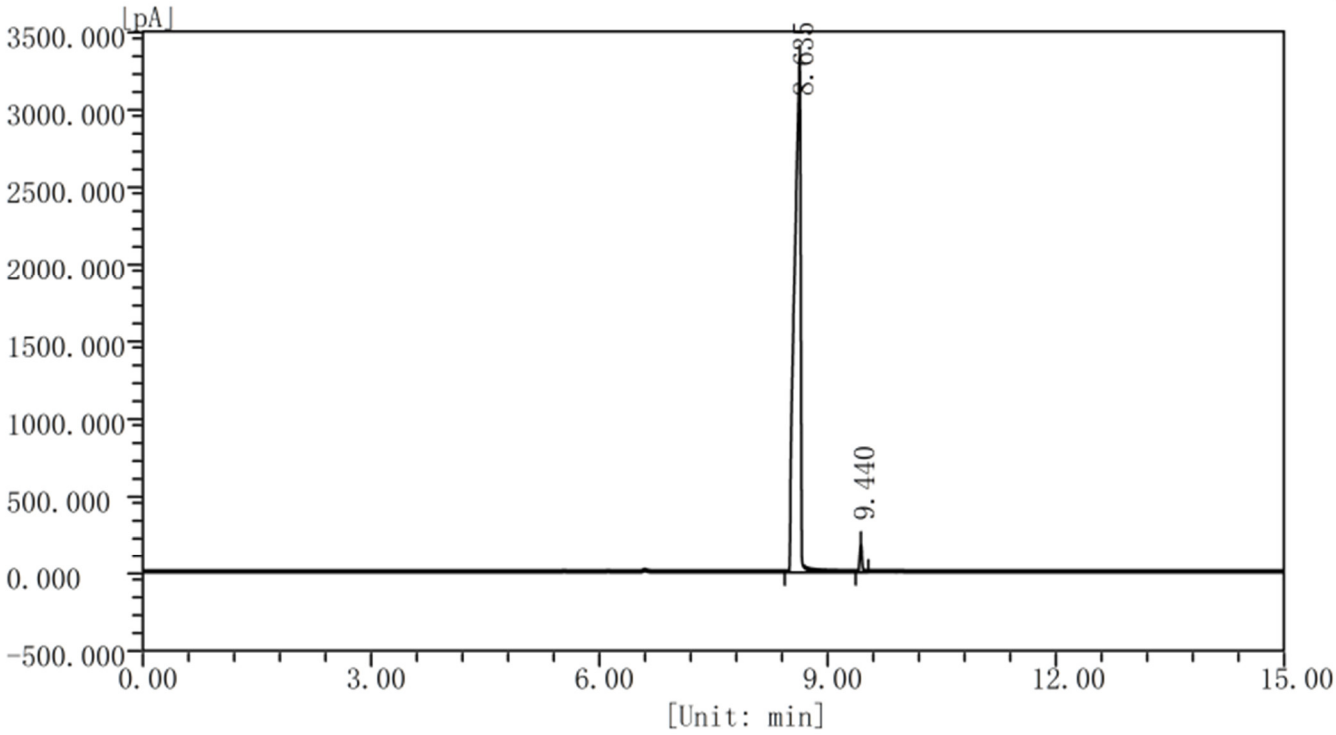
Supplementary Figure 61. GC analysis of the 98:2 **Cy**/**Bz** after adsorption by **H-TCNB***α* (6.00 mg).



分析结果

峰序	组分名	保留时间 [min]	峰高 [uV]	峰面积 [uV*s]	峰面积 [%]	含量 [%]
1	苯	6.349	20552.9	71933.7	0.2720	0.2720
2	环己烷	6.653	6050902.8	26372177.1	99.7280	99.7280
		总计:	6071455.5	26444110.0	100.0000	100.0000

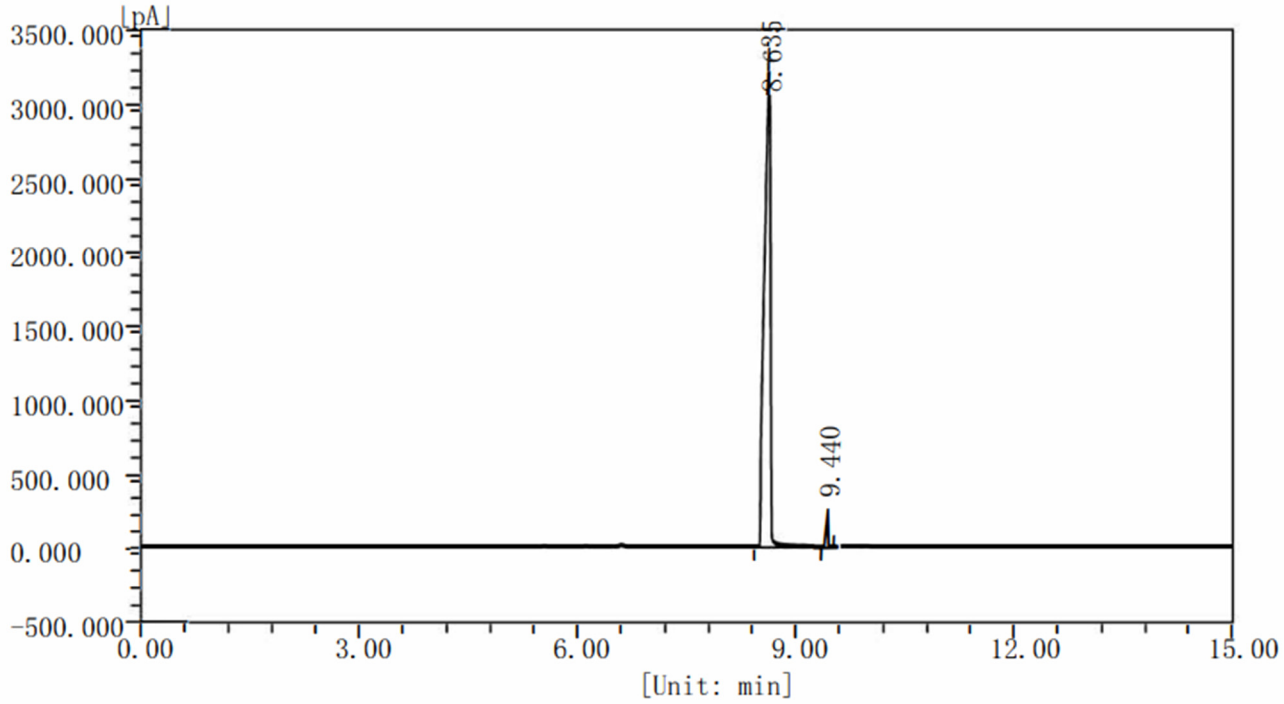
Supplementary Figure 62. GC analysis of the 98:2 **Cy**/**Bz** after adsorption by **H-TCNB*α*** (9.00 mg).



分析结果

峰序	组分名	保留时间 [min]	峰高 [uV]	峰面积 [uV*s]	峰面积 [%]	含量 [%]
1	吡啶	8.635	3330020.8	18631926.3	97.9385	97.9385
2	甲苯	9.440	186273.1	392189.2	2.0615	2.0615
		总计:	3516294.0	19024116.0	100.0000	100.0000

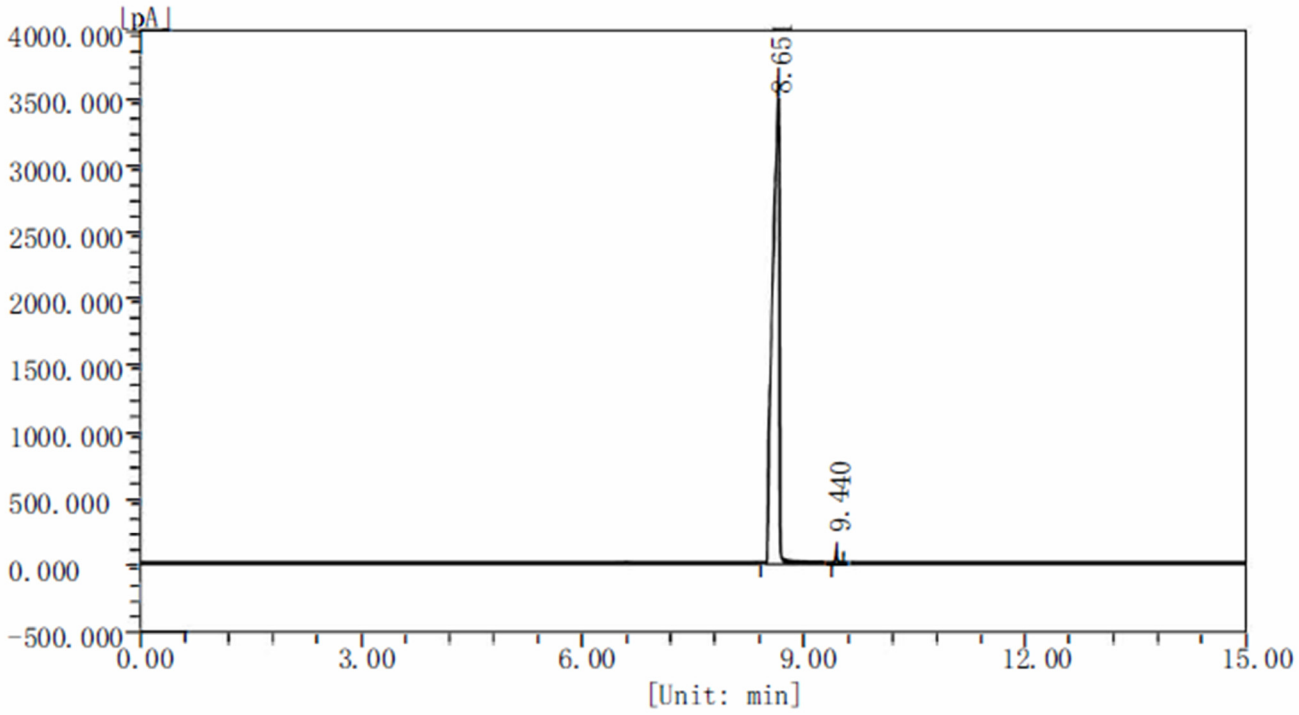
Supplementary Figure 63. GC analysis of 98:2 **Py**/**Tol**.



分析结果

峰序	组分名	保留时间 [min]	峰高 [uV]	峰面积 [uV*s]	峰面积 [%]	含量 [%]
1	吡啶	8.635	3870305.7	21654895.2	98.4877	98.4877
2	甲苯	9.440	164584.2	346524.3	1.5123	1.5123
		总计:	4034890.0	22001420.0	100.0000	100.0000

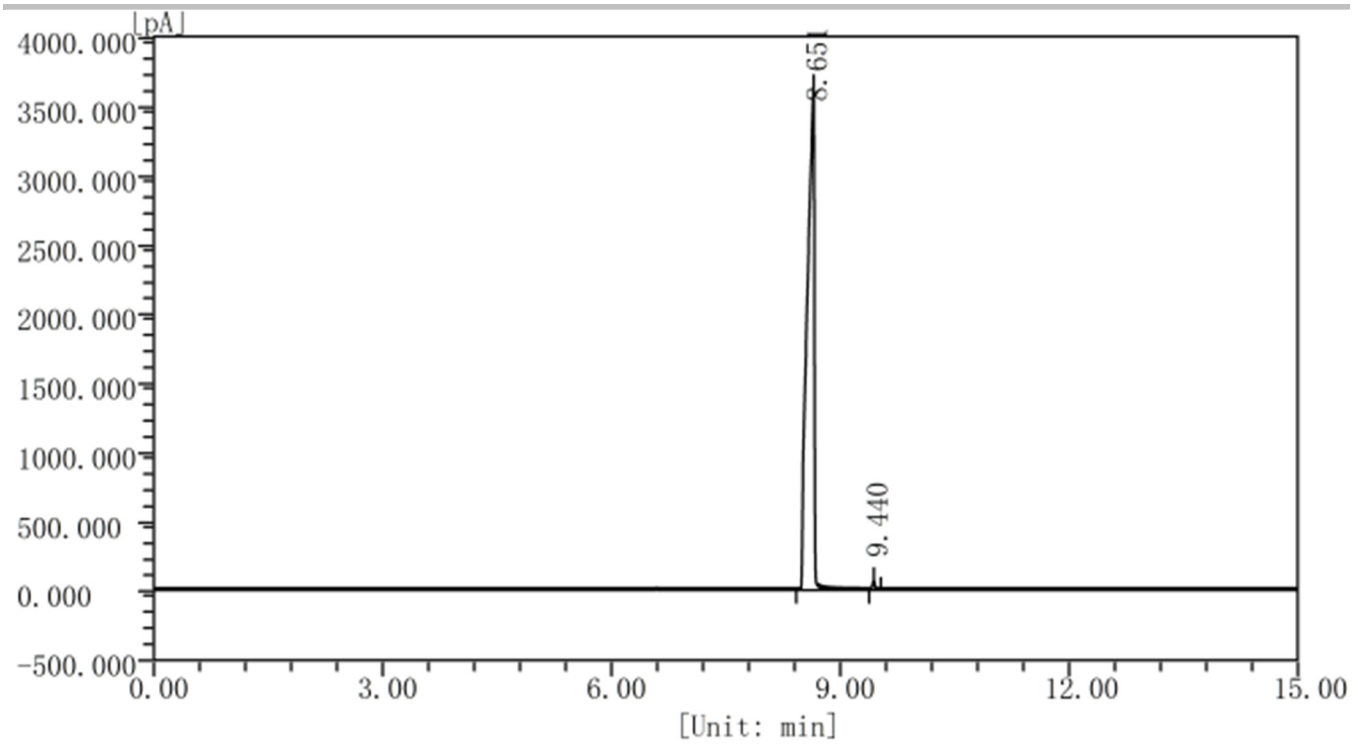
Supplementary Figure 64. GC analysis of the 98:2 **Py**/**Tol** after adsorption by **H-TCNB***α* (3.00 mg).



分析结果

峰序	组分名	保留时间 [min]	峰高 [uV]	峰面积 [uV*s]	峰面积 [%]	含量 [%]
1	吡啶	8.651	401293.7	22452941.3	99.0421	99.0421
2	甲苯	9.440	95666.5	201421.4	0.9579	0.9579
		总计:	496960.2	22654362.7	100.0000	100.0000

Supplementary Figure 65. GC analysis of the 98:2 **Py**/**Tol** after adsorption by **H-TCNB*α*** (6.00 mg).

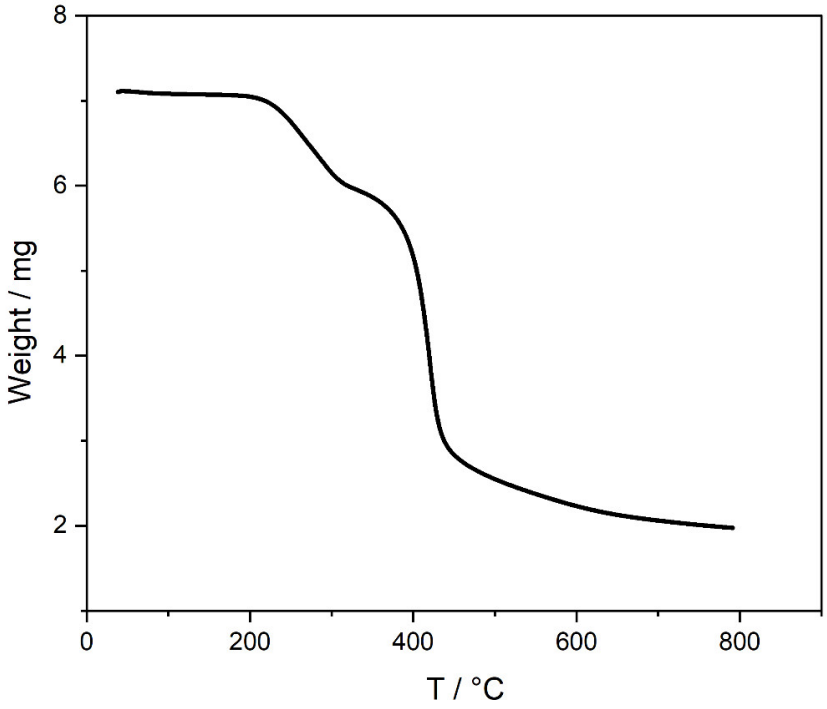


分析结果

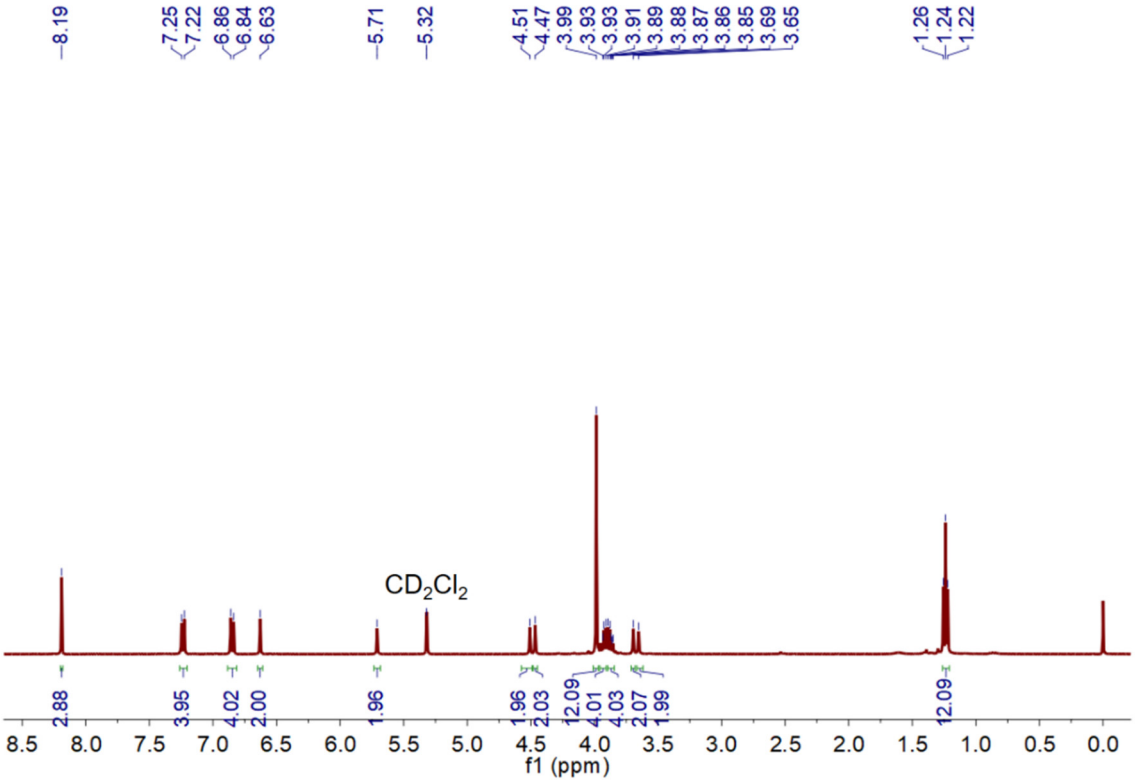
峰序	组分名	保留时间 [min]	峰高 [uV]	峰面积 [uV*s]	峰面积 [%]	含量 [%]
1	吡啶	8.651	3638153.3	23316906.7	99.3540	99.3540
2	甲苯	9.440	69336.0	151597.3	0.6460	0.6460
		总计:	3707489.3	23468504.0	100.0000	100.0000

Supplementary Figure 66. GC analysis of the 98:2 **Py**/**Tol** after adsorption by **H-TCNB*α*** (9.00 mg).

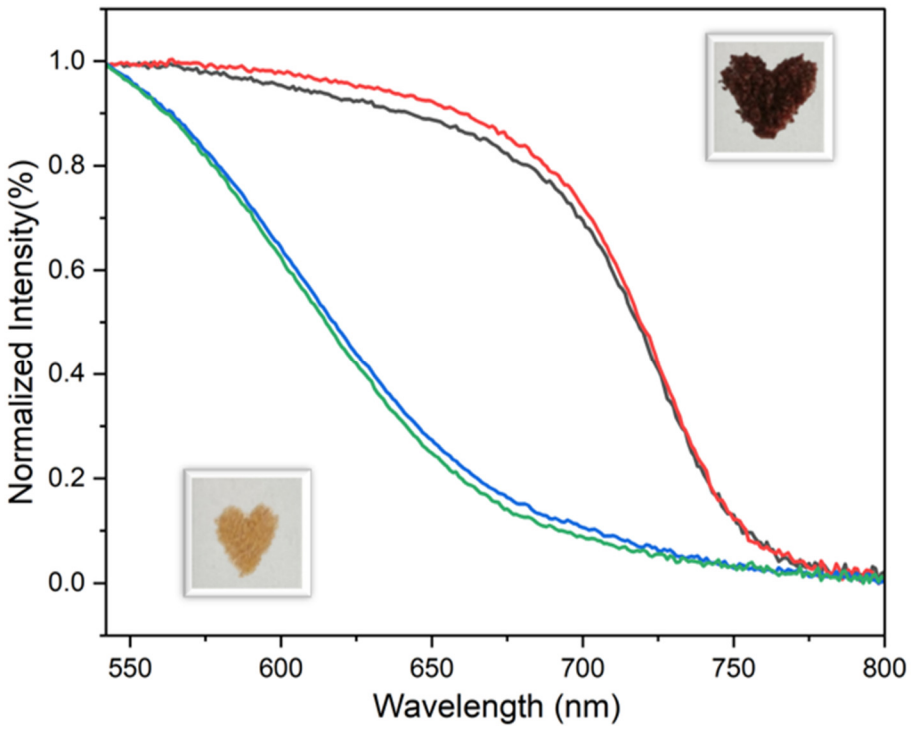
11. Recyclability of H-TCNB*α*



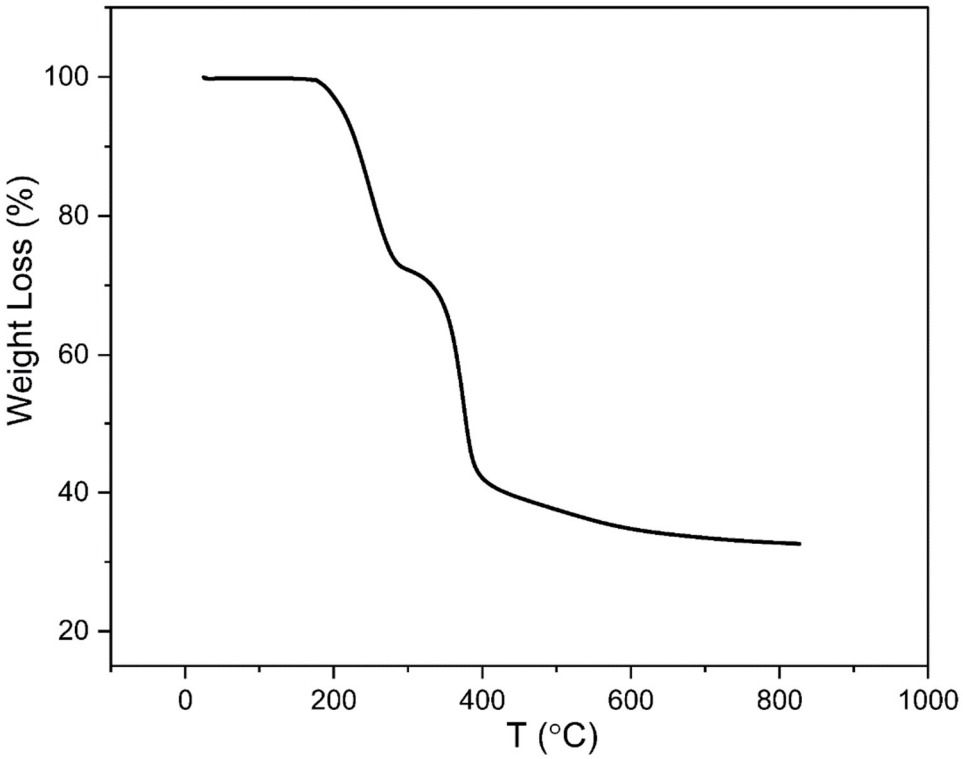
Supplementary Figure 67. Thermogravimetric analysis of **H-TCNB@Bz** after heating at 100 °C under vacuum for 9 h.



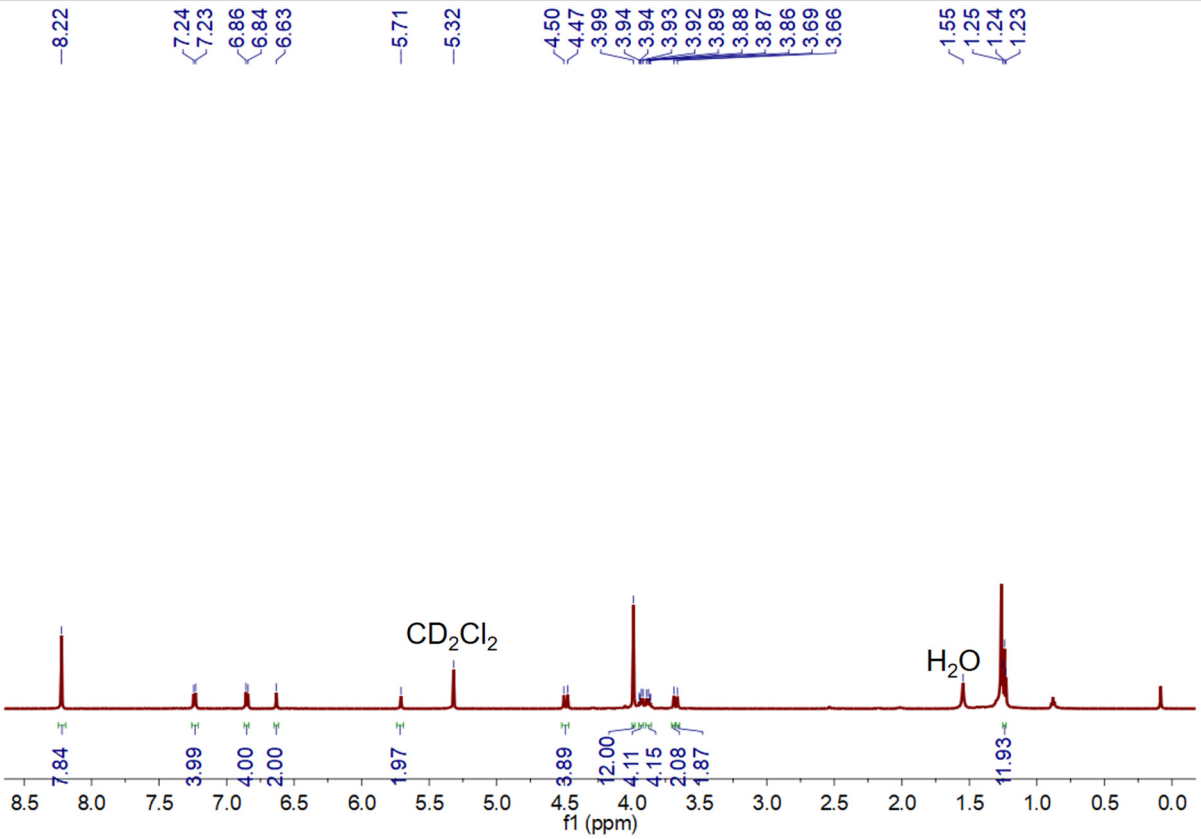
Supplementary Figure 68. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H-TCNB@Bz** after heating at 100 °C under vacuum for 9 h.



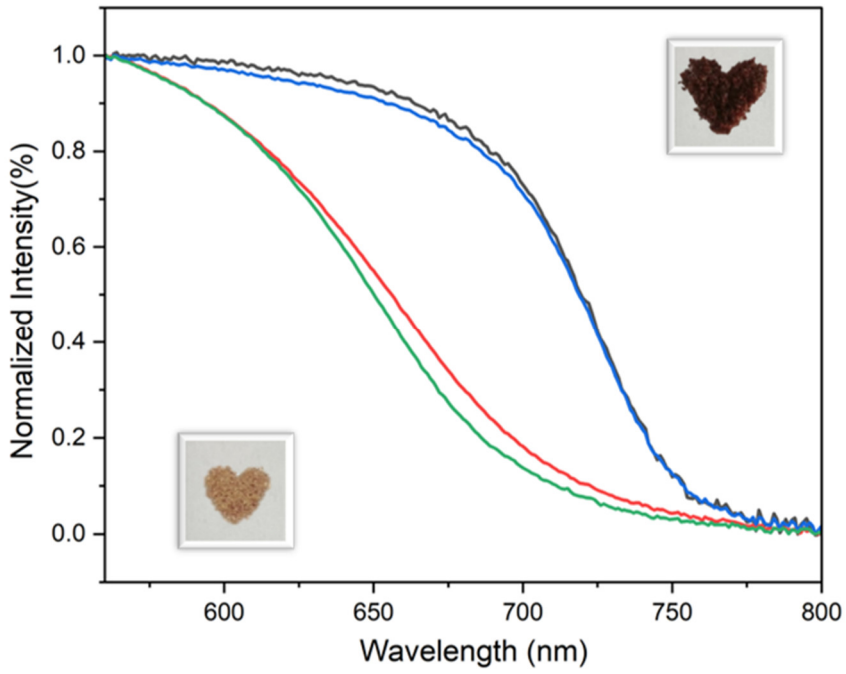
Supplementary Figure 69. Diffuse reflectance spectra of **H-TCNB*α*** (black line), re-activated **H-TCNB*α*** (red line), first uptake of **Bz** (blue line), and second uptake of **Bz** (green line).



Supplementary Figure 70. Thermogravimetric analysis of **H-TCNB@Tol** after heating at 100 °C under vacuum for 9 h.



Supplementary Figure 71. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 293 K) of **H-TCNB@Tol** after heating at 100 °C under vacuum for 9 h.



Supplementary Figure 72. Diffuse reflectance spectra of **H-TCNB*α*** (black line), re-activated **H-TCNB*α*** (red line), first uptake of **Tol** (blue line), and second uptake of **Tol** (green line).

12. References

1. Zhou, J., Yu, G., Li, Q., Wang, M. & Huang, F. Separation of benzene and cyclohexane by nonporous adaptive crystals of a hybrid[3]arene. *J. Am. Chem. Soc*. **142**, 2228–2232 (2020).