Supporting Information

Polar Organic Cages for Efficient Azeotropic Mixtures Separation

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Materials and Methods

All reagents were commercially available and used as supplied without further purification. Compound **DIHO-cage** was synthesized by modifying the previous literature report.[1]

Single Crystal Growth.

Single crystals of **DIHO-cage@DCM** and **DIHO-cage@CHCl₃** were obtained by vapor diffusion of acetonitrile into DCM and chloroform solution of **DIHO-cage** at room temperature respectively; Colourless and suitable single crystals of **DIHO-cage@Tol** and **DIHO-cage@Py** were also obtained after 3 days by vapor diffusion of acetonitrile into **DCM/Tol** and **DCM/Py** solutions of **DIHO-cage** at room temperature respectively.

Single X-ray Crystal Structure Determination

Single crystal X-ray diffraction data were recorded on a Bruker D8 Venture and Metaljet equipped with a digital camera diffractometer using graphite-monochromated CuKα radiation (λ= 1.5418 Å) and GaKα radiation (λ= 1.34139 Å) respectively for the crystal structures. Data reductions were carried out by means of a standard procedure using the Bruker software package SaintPlus 6.01.[2] The absorption corrections and the correction of other systematic errors were performed using SADABS.[3] The structures were solved by direct methods using SHELXS-2008 and refined using SHELXL-2018.[4] X-Seed[5] and OLEX2[6] were used as the graphical interface for the SHELX program suite. Anisotropic thermal parameters were applied to all non-hydrogen atoms. All the

hydrogen atoms were generated geometrically. Data collection, structure refinement parameters and crystallographic data for the crystals are given in Table S1.

Activation of DIHO-cage.

Crystalline **DIHO-cage** materials were activated under vacuum at 40 °C for 2 h to obtain the activated **DIHO-cage**. While the activated **DIHO-cage** after adsorption of **Tol** was regenerated by releasing the adsorbed guests upon heating at 70 °C under vacuum for 3 h. Alternatively, the **DIHO-cage** was also regenerated after adsorption by first washing with n-hexane and then activated at much lower temperature of 45 °C under vacuum for 1 h.

Solid-vapor Adsorption Experiments.

An open 5 mL vial containing 10 mg of activated **DIHO-cage** was placed in a 20 mL vial containing 1 mL of each solvent and an equal volume 1:1 (v/v) binary mixture of **Tol/Py**. We also investigated the adsorption of **Tol** at much lower ratio of 1:3 (v/v) binary mixture of **Tol/Py**.

NMR

NMR spectra were recorded on Bruker-400 (400 MHz for ^{1}H; 101 MHz for ^{13}C) instruments internally referenced to $SiMe_4$ signal.

PXRD

Powder X-ray diffraction (PXRD) patterns were obtained using a XRD Bruker D8-ADVANCE X-ray diffractometer (40 KV, 40 mA) with the Cu Kα radiation (λ = 1.5418 Å). Data were measured over the range of 3.5−40° in 2°/min steps. The sample was placed in a zero-background sample holder and normal configuration of the instrument was used.

GC-MS

Gas chromatography (GC) analysis. GC measurements were carried out using an Agilent 7890A instrument configured with an FID detector and a DB-VRX column (60 m × 0.250 mm × 0.14 µm). The following GC method was used: the oven was programmed from 70 °C, and ramped in 10 °C min^{-1} increments to 150 °C with 15 min hold; the total run time was 25 min; injection

temperature was 250 °C; detector temperature was 250 °C with hydrogen, air, and make-up flow-rates of 40, 400, and 15 mL min^{-1}, respectively; helium (carrier gas) flowrate was 3.0 mL min^{-1}.

TGA

Thermogravimetric analysis was carried out using an automatic sample loading TA Instruments Q50 analyzer. The samples were heated starting at room temperature to 700 °C using nitrogen as the protective gas.

BET Analysis

Low-pressure gas adsorption measurements were performed on a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP) 2020 surface area analyzer. Sample was degassed under dynamic vacuum for 5 h at 40 °C prior to each measurement. N_2 isotherm was measured using a liquid nitrogen bath (77 K). CO_2 isotherm was also measured at 196 K.

Synthesis of DIHO-cage

Tris(2-aminoethyl) amine (Tren) (292.48 mg; 2.0 mmol) was dissolved in MeCN (5 mL) and was added dropwise over 1 h to the solution of 2,5 Dihydroxyterephthalaldehyde (498.39 mg; 3.0 mmol) in MeCN (50 mL). The reaction mixture was stirred overnight at room temperature. A light-yellow precipitate was formed which was filtered and washed further with MeCN, then dissolved in dichloromethane and filtered to remove polymers. After the removal of dichloromethane, **DIHO-cage** was obtained in 70% yield.
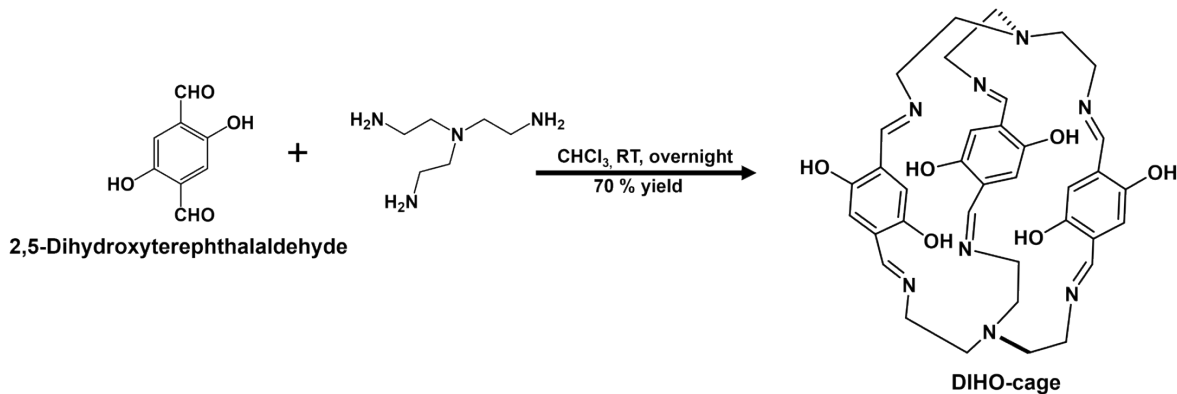
Scheme S1: Synthesis of **DIHO-cage**.
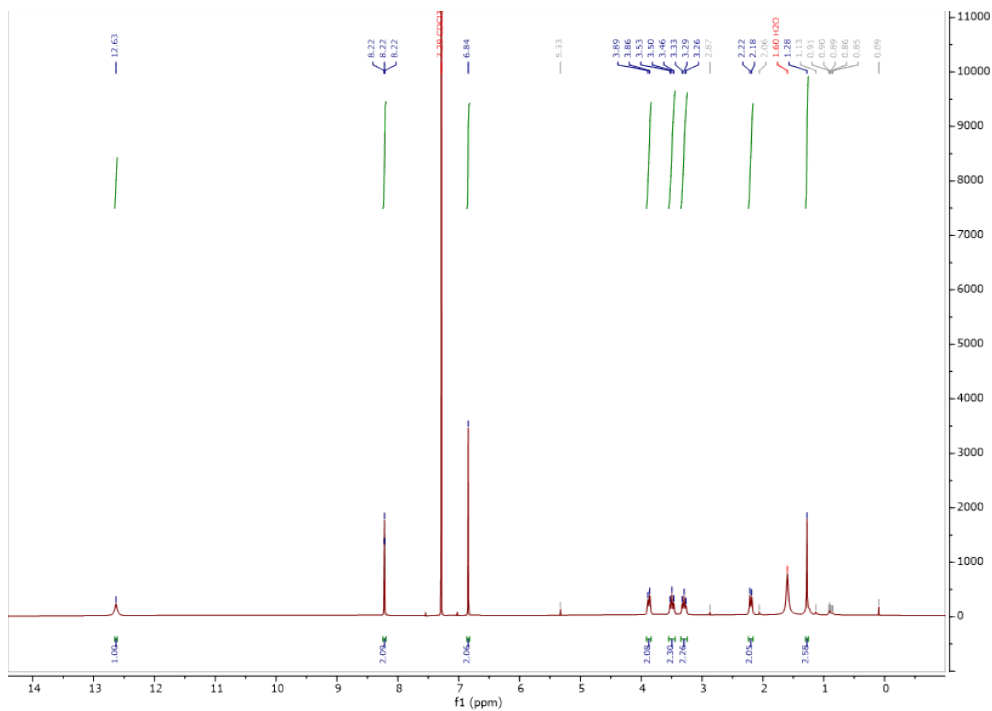
Figure S1a: ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 293 K) of the **DIHO-cage**.
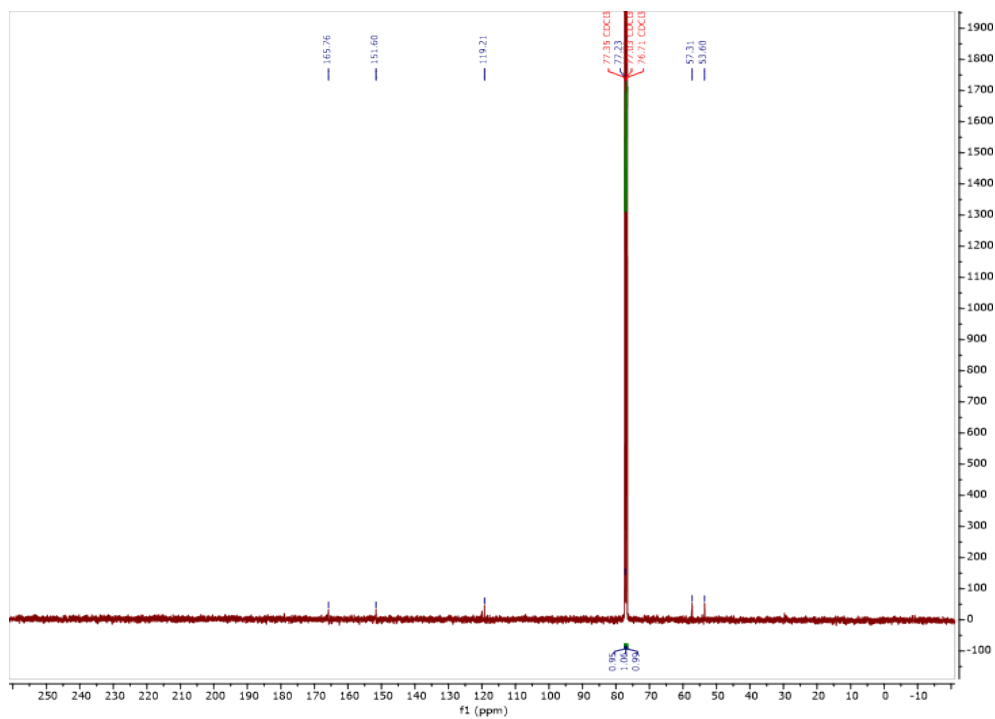
Figure S1b: ^{13}C NMR spectrum (101 MHz, 298K, CDCl$_3$) of the **DIHO-cage**.

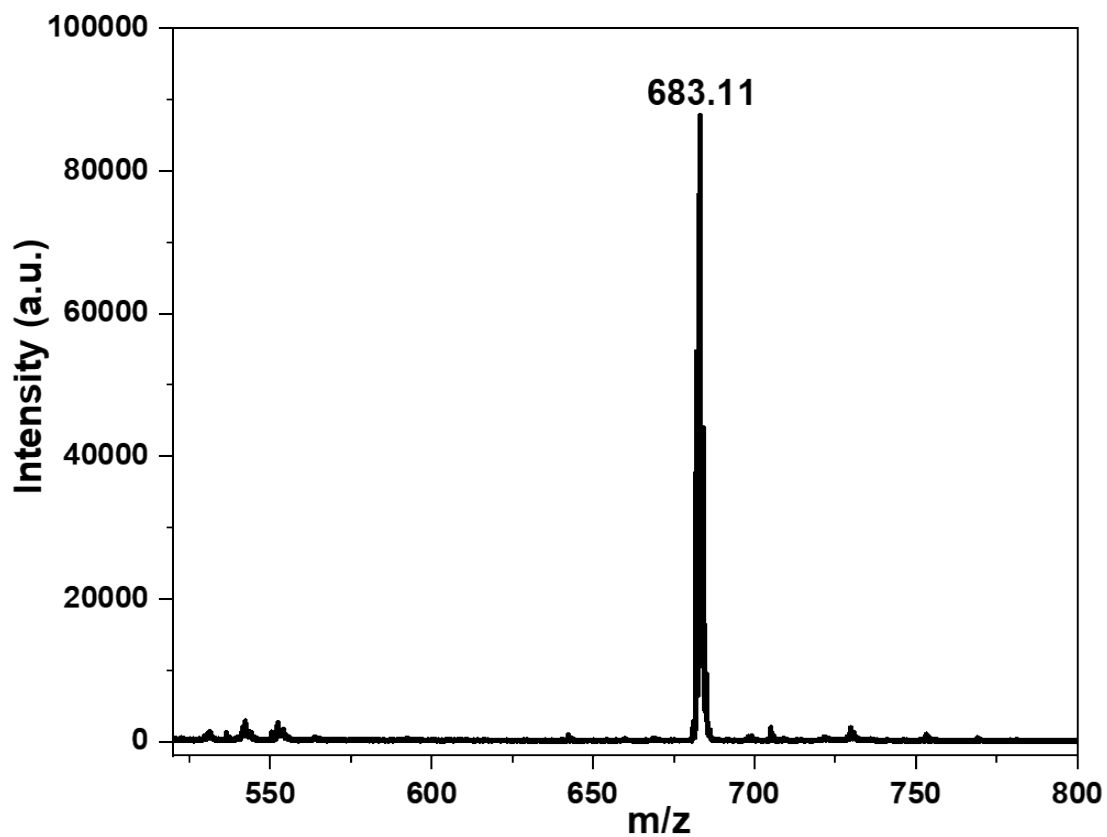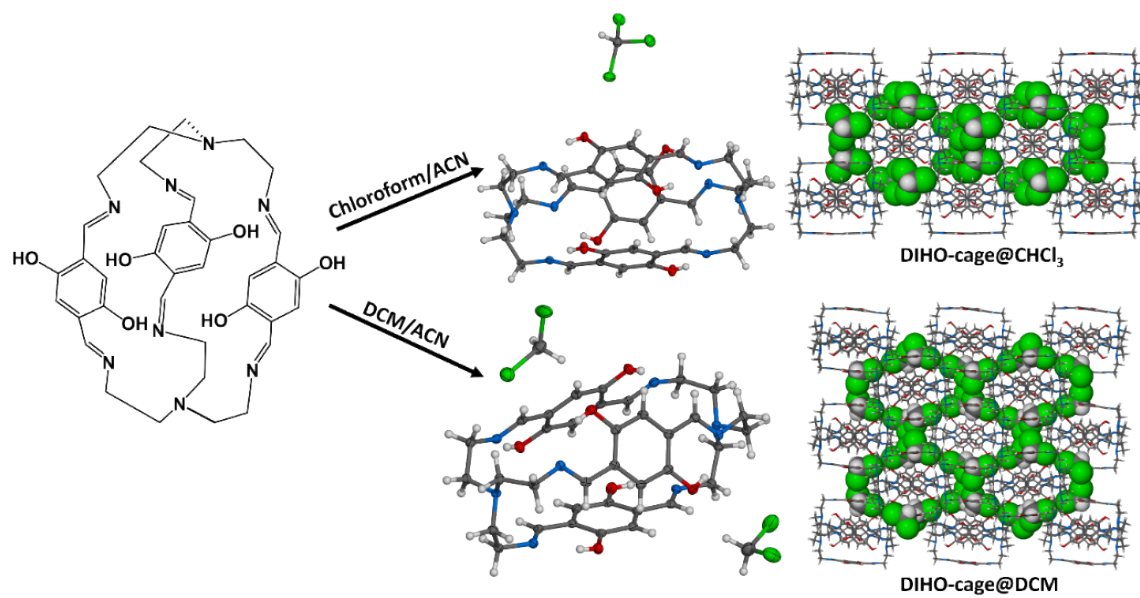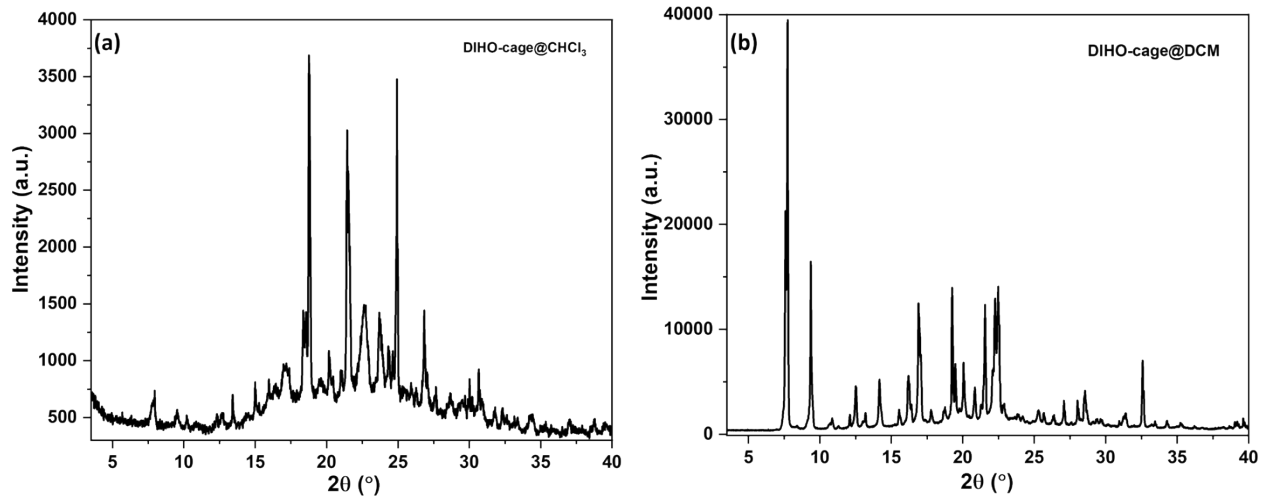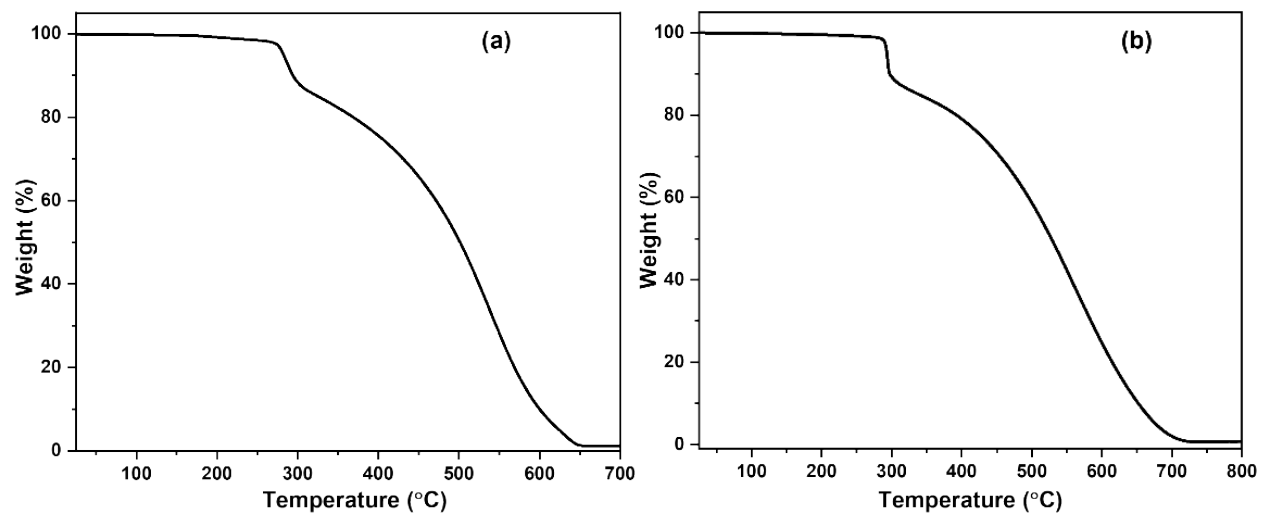**Figure S2:** ESI-Mass spectrum of the **DIHO-cage**.

Figure S3a: Crystallization of **DIHO-cage** in Chloroform (**DIHO-cage@CHCl₃**) and DCM (**DIHO-cage@DCM**).

Figure S3b: PXRD patterns of **DIHO-cage** in **(a)** Chloroform (**DIHO-cage@CHCl₃**) and **(b)** DCM (**DIHO-cage@DCM**).

Figure S4: TGA curves of **(a)** assynthesized and **(b)** fully activated **DIHO-cage**.
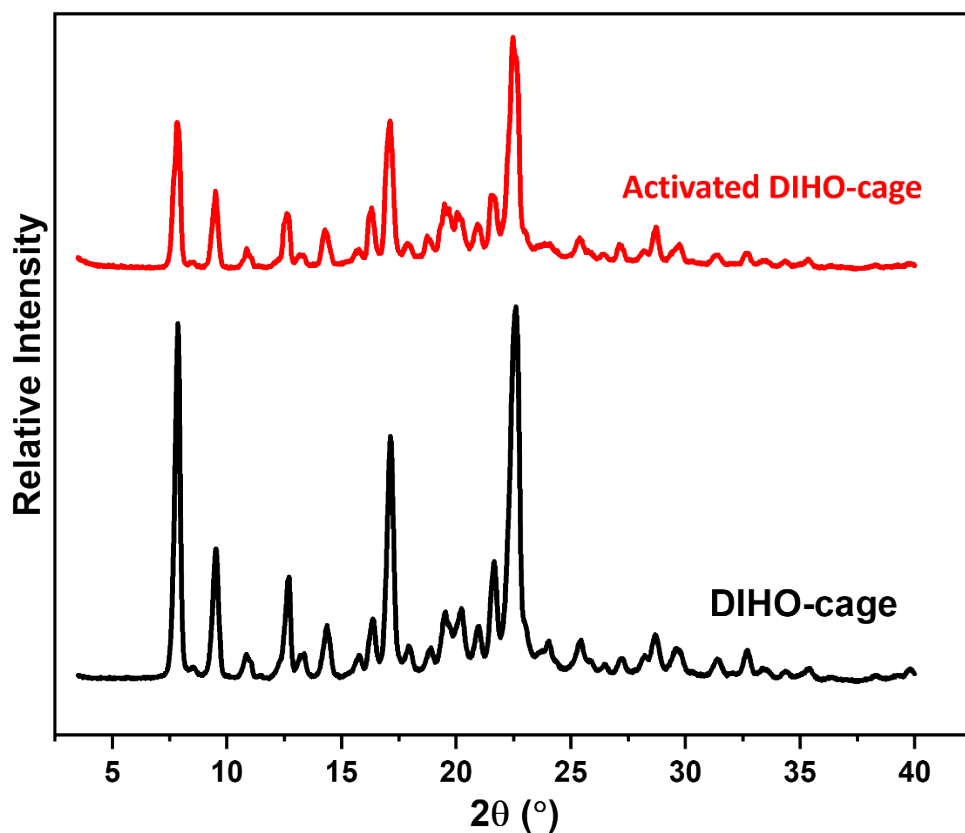
Figure S5: PXRD patterns of the assynthesized and activated **DIHO-cage.**
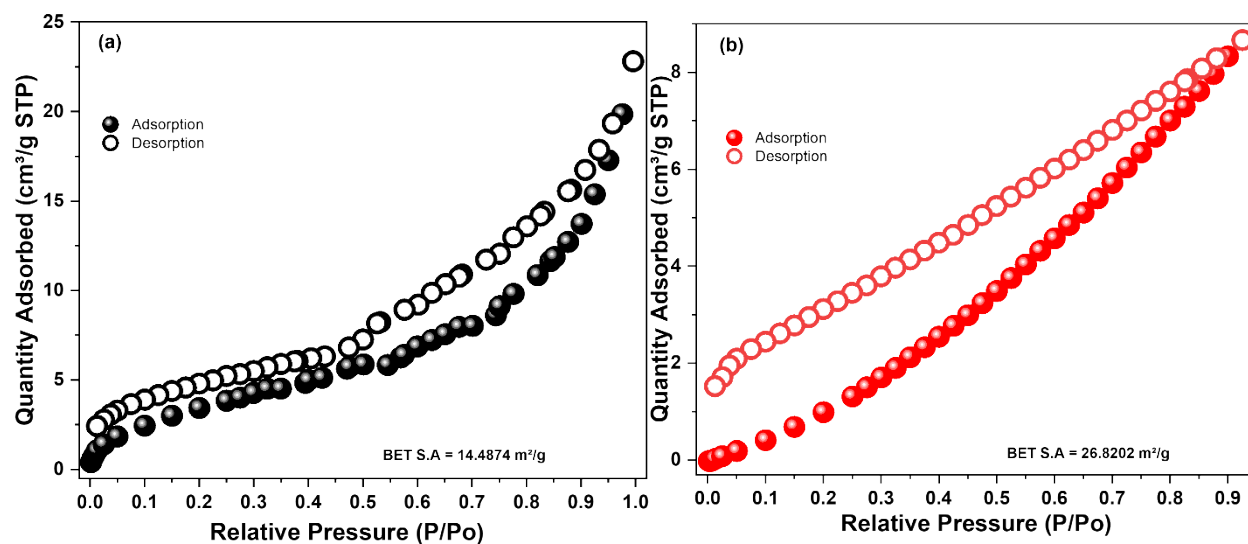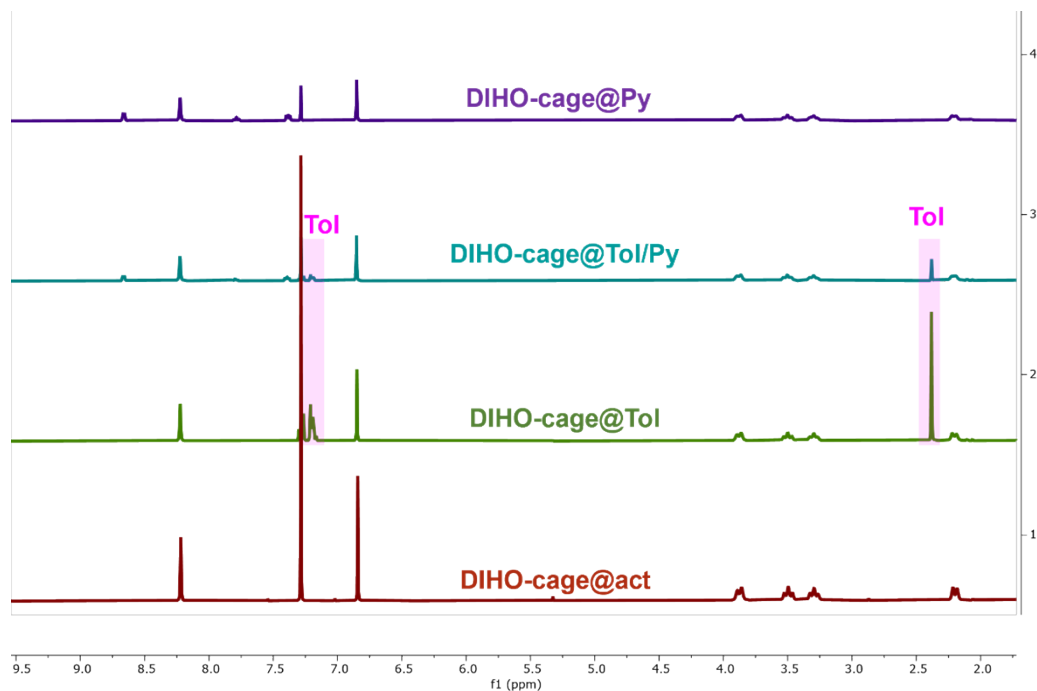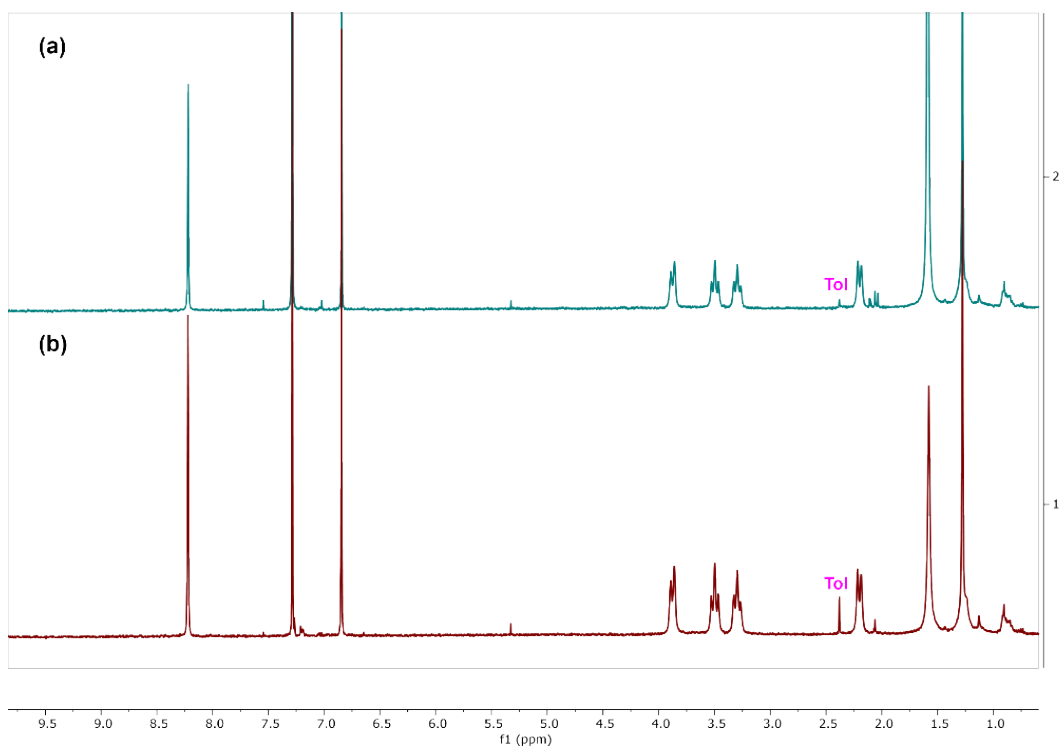

Figure S6: (a) Nitrogen gas sorption isotherm at 77 K and **(b)** CO_2 gas isotherm at 196 K for activated DIHO-cage.
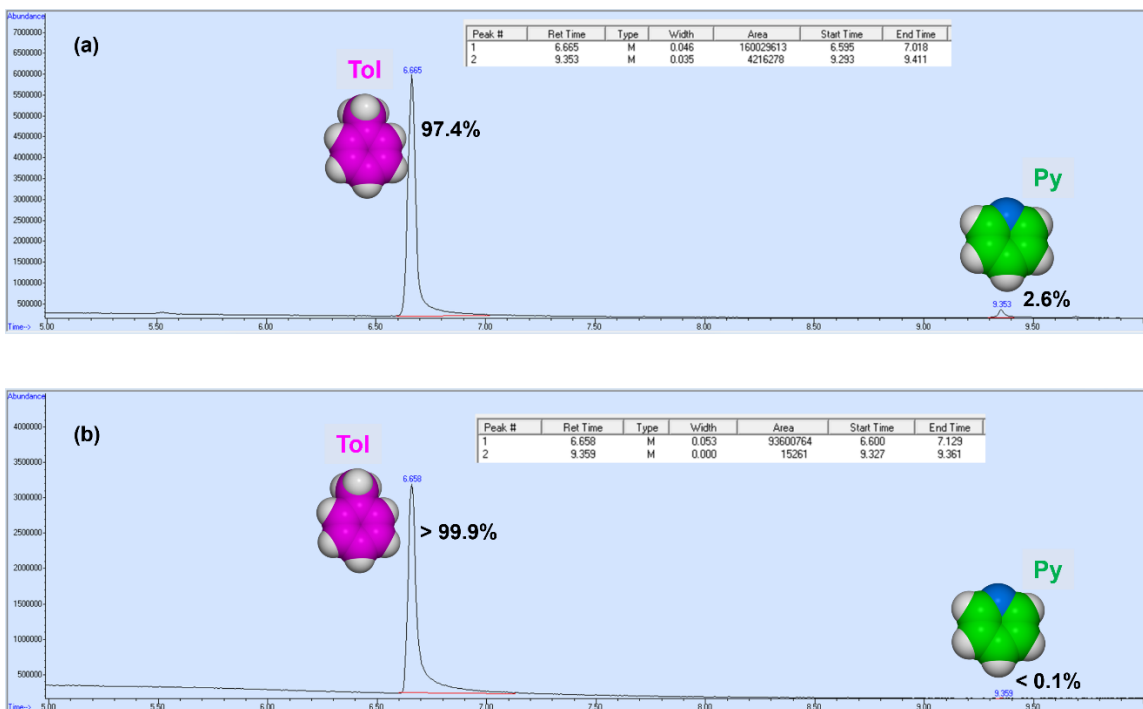
Figure S7: ^{1}H-NMR spectra (400 MHz, CDCl3, 293 K) showing the adsorption of **Tol** and **Py** by activated DIHO-cage after 24 h exposure.
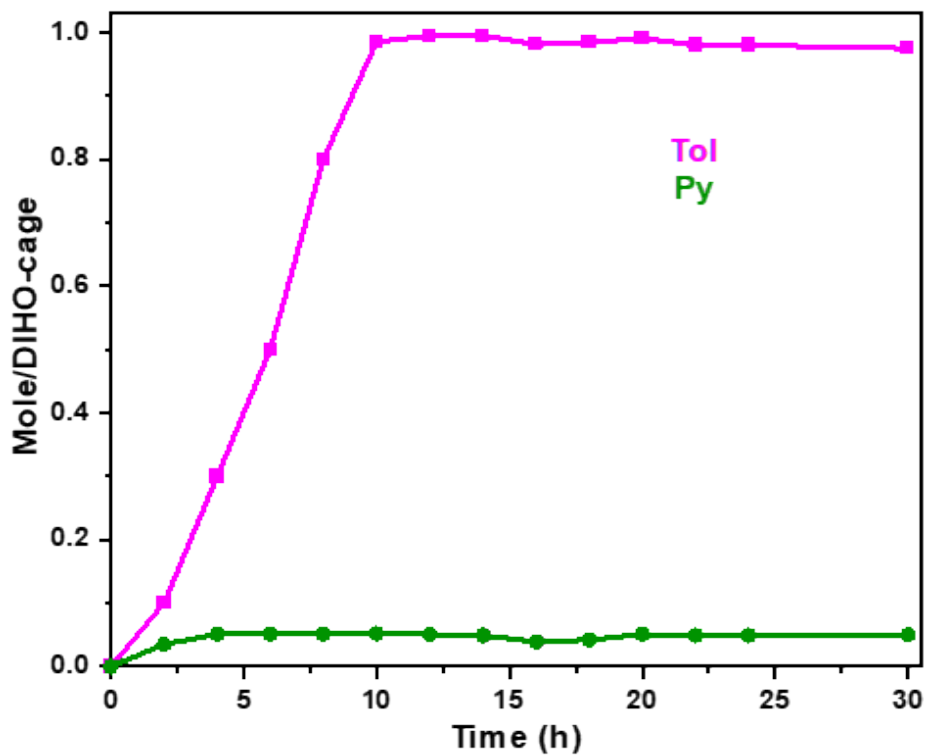

Figure S8: Magnified ^{1}H-NMR spectra showing the uptake of **Tol** from **Tol/Py** (a) 1:3 (v/v) and (b) 3:1(v/v) binary mixture by activated DIHO-cage after 24 h.
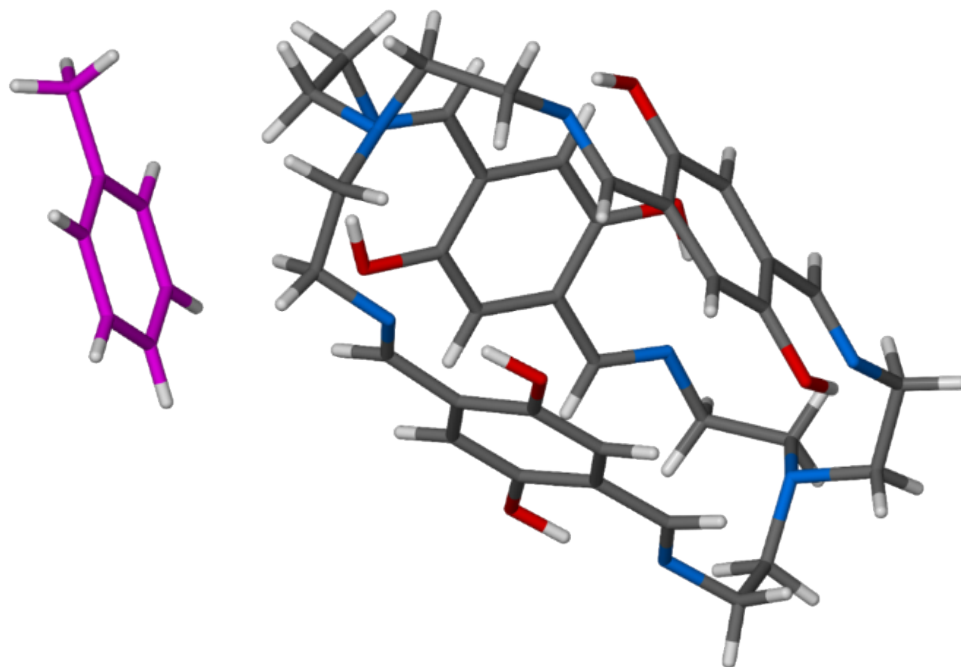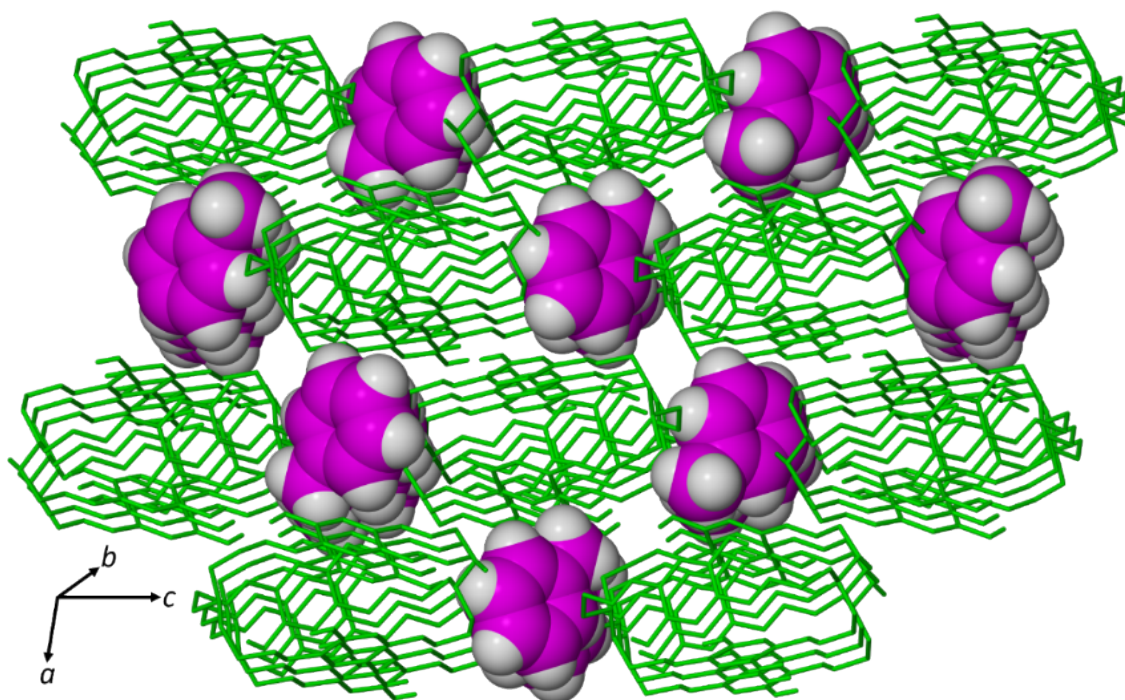
Figure S9: Relative amount of **Tol** and **Py** adsorbed from **(a)** 1:3 (v/v) and **(b)** 3:1 (v/v) Tol/Py mixtures by activated DIHO-cage as determined by gas chromatography.
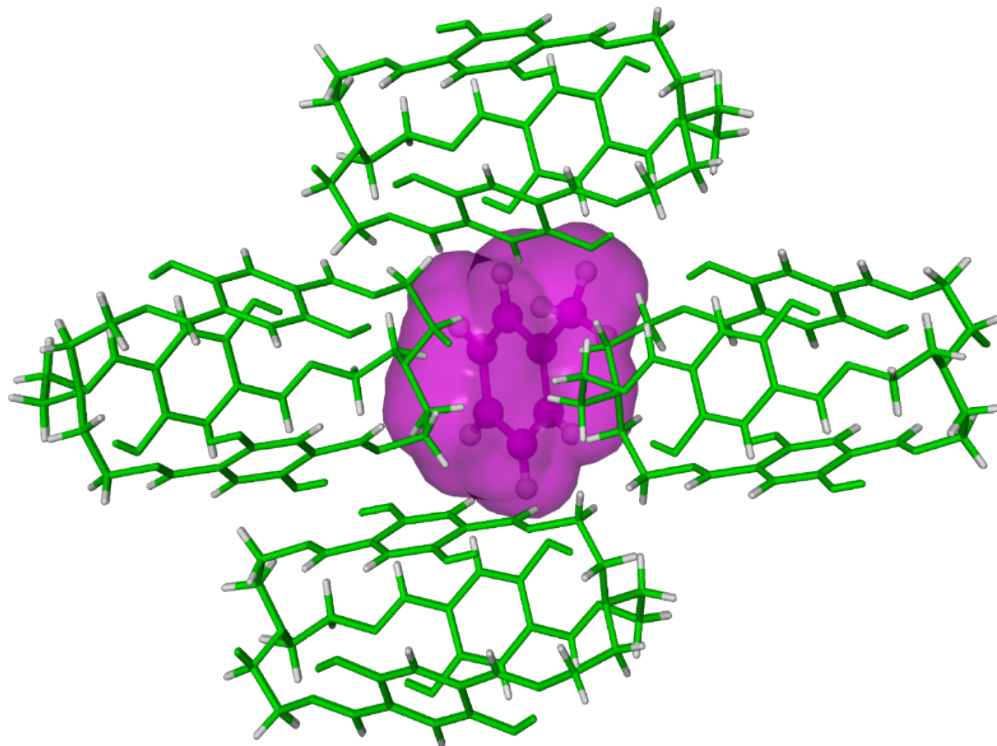

Figure S10: Time-dependent solid-vapor sorption plot for the 1:1 (v/v) of **Tol/Py** mixture by activated DIHO-cage.
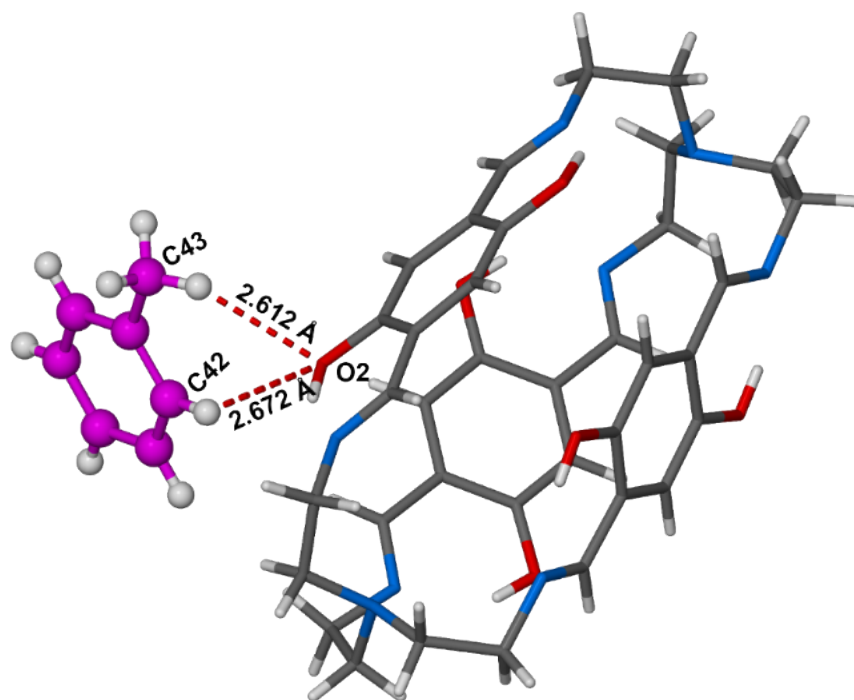
Figure S11: Asymmetric unit of the Crystal structure of **DIHO-cage@Tol** showing 1:1 host/guest ratio.
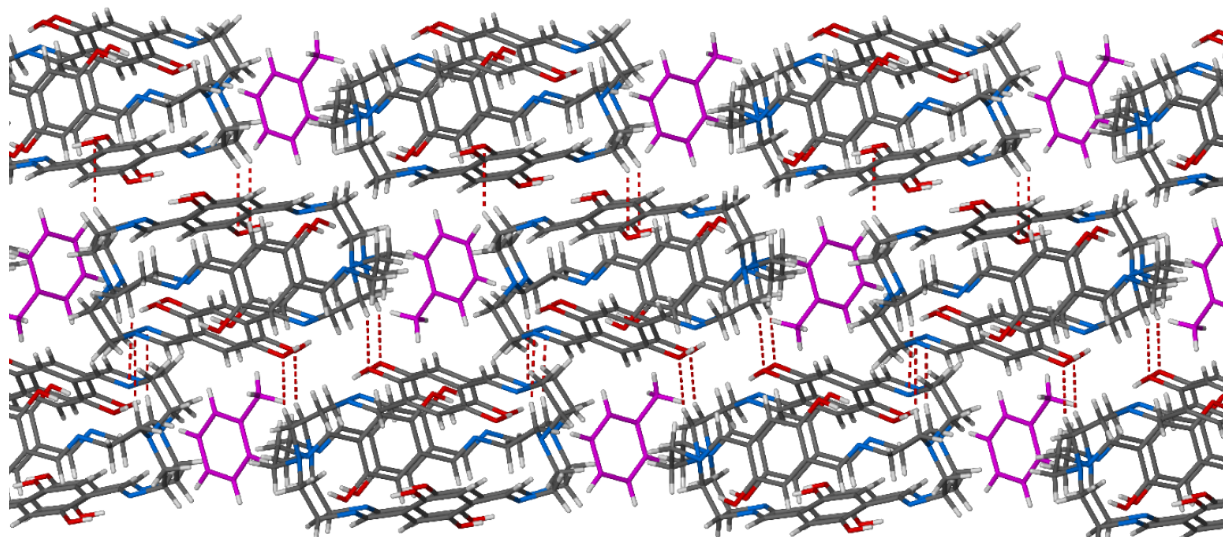

Figure S12a: Perspective view showing **Tol** (pink) in the channel of the crystal packing of **DIHO-cage@Tol** when viewed along *b*-axis.

Figure S12b: Crystal packing showing the **Tol** guest (pink) occupied void using MSRoll program[7] when viewed along the crystallographic *b*-axis.

Figure S13: Crystal structure showing the C–H···O host-guest intermolecular interactions between **DIHO-cage** and **Tol** in **DIHO-cage@Tol** when viewed along *a*-axis.

Figure S14: Perspective view showing C–H⋯O and C–H⋯N intermolecular hydrogen bonding interactions between the cages in **DIHO-cage@Tol** crystal structure.
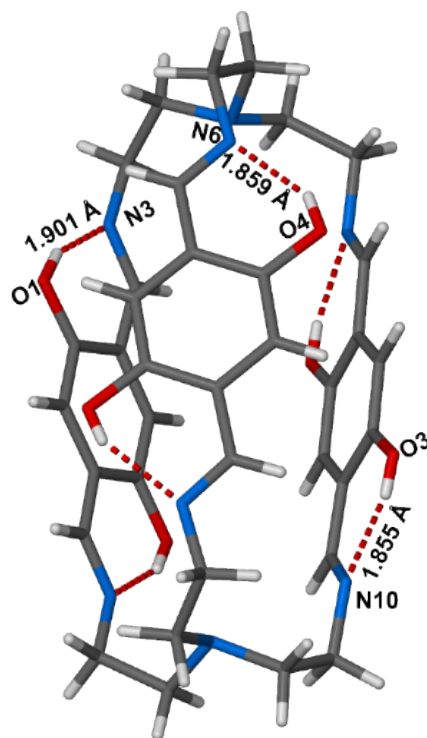
Figure S15: Perspective view showing very strong O–H⋯N intramolecular hydrogen bonding interactions within the cage in **DIHO-cage@Tol** crystal structure.
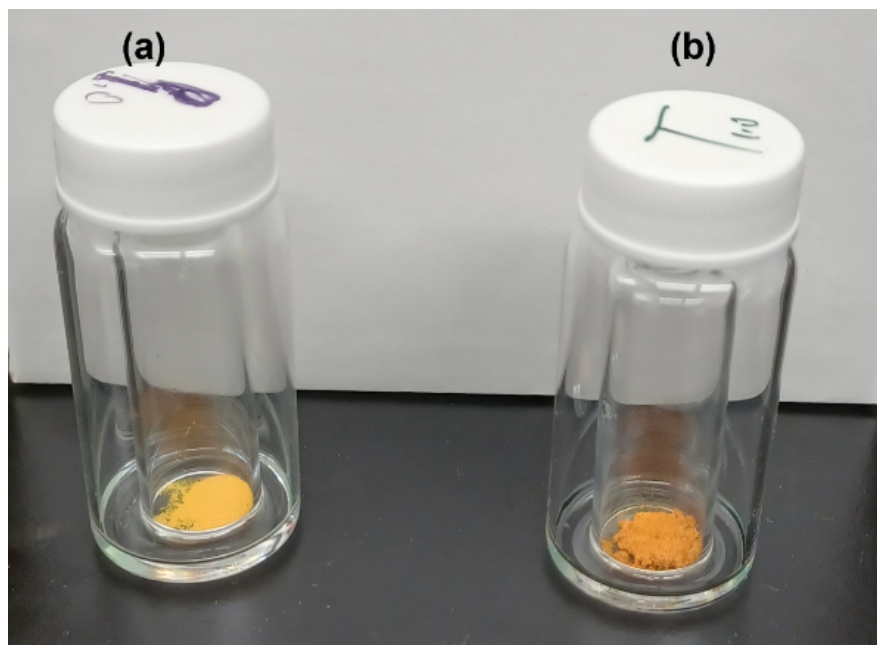
Figure S16: Images of solid-vapor adsorption of **(a)** pyridine and **(b)** toluene by the **DIHO-cage** after 24 h showing a vapochromic behaviour.
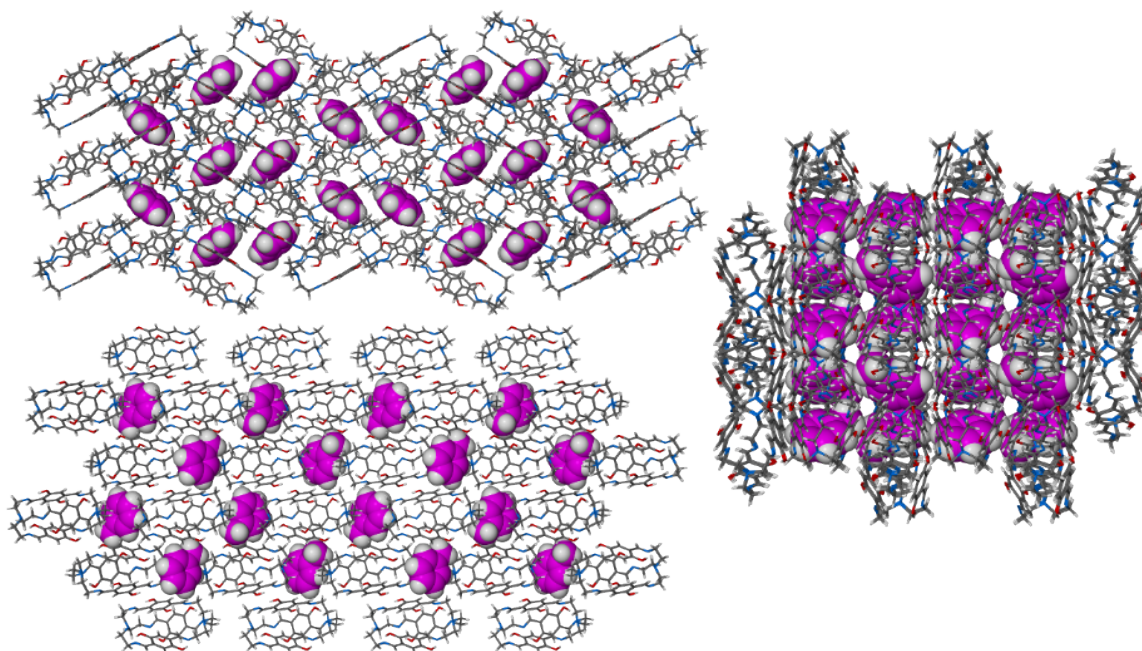
Figure S17: Crystal packing of **DIHO-cage@Tol** when viewed along all the three crystallographic axes.
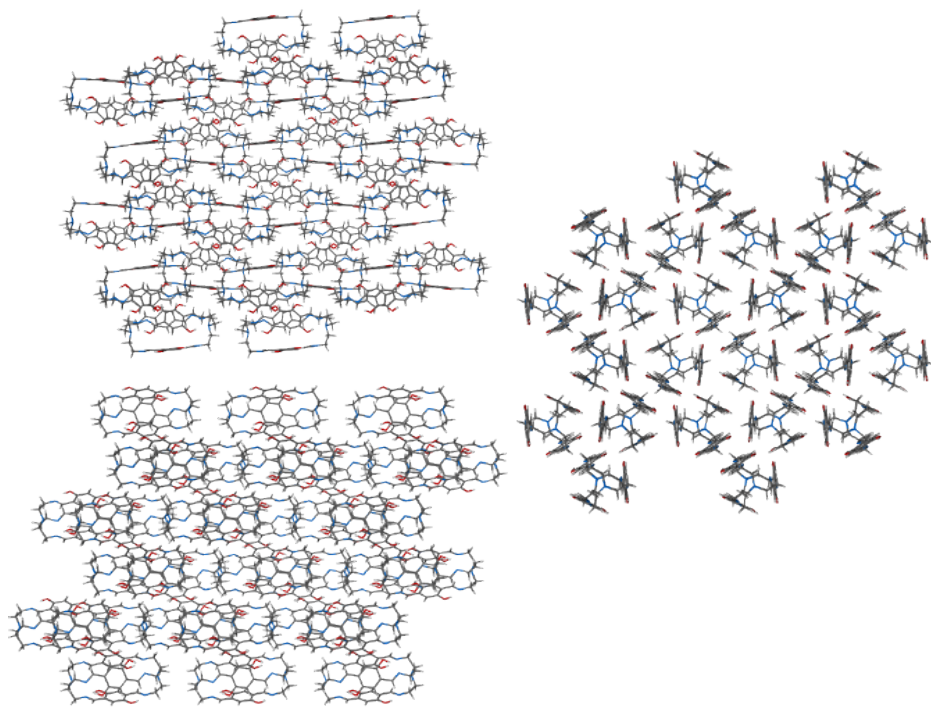
Figure S18: Crystal packing of **DIHO-cage@Py** when viewed along all the three crystallographic axes.
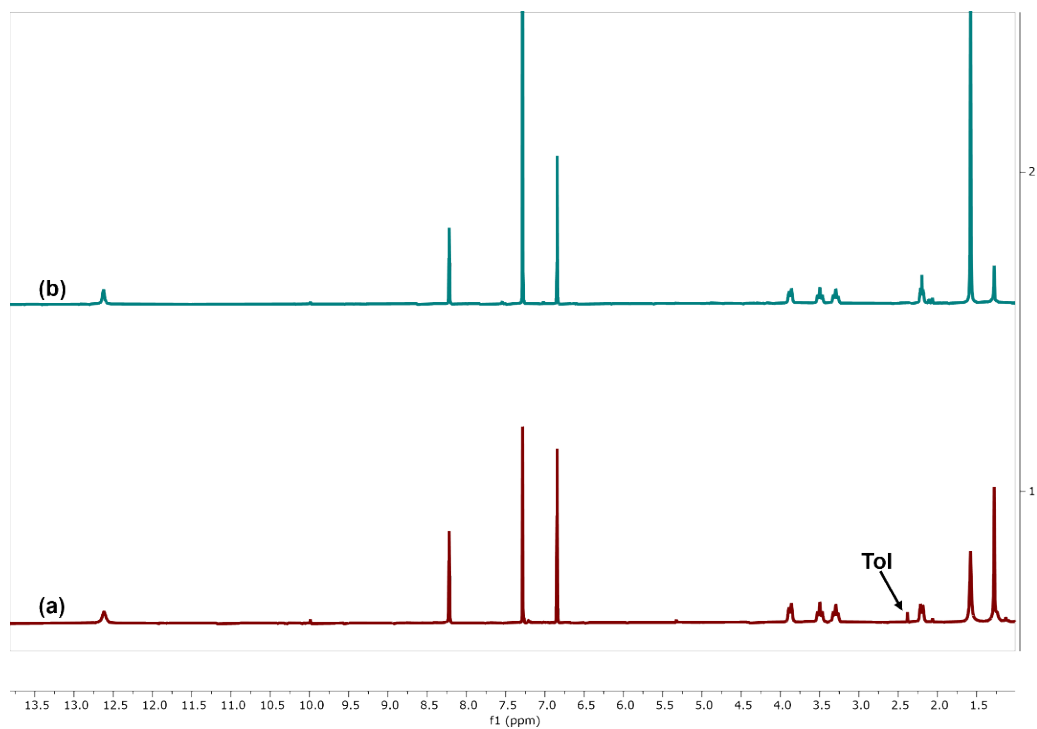
Figure S19: ¹H-NMR spectra (400 MHz, CDCl₃, 293 K) showing **(a) DIHO-cage@Tol; (b)** Regenerated **DIHO-cage** after washing with n-hexane and heated at 45 °C under vacuum for 1 h.

Figure S20: PXRD pattern of the regenerated DIHO-cage.

Figure S21: (a) Relative amount of **Tol** and **Py** in 1:1 (v/v) equimolar mixture of **Tol/Py** and **(b)** relative uptake of **Tol** and **Py** by **DIHO-cage** after adsorption as determined by gas chromatography.
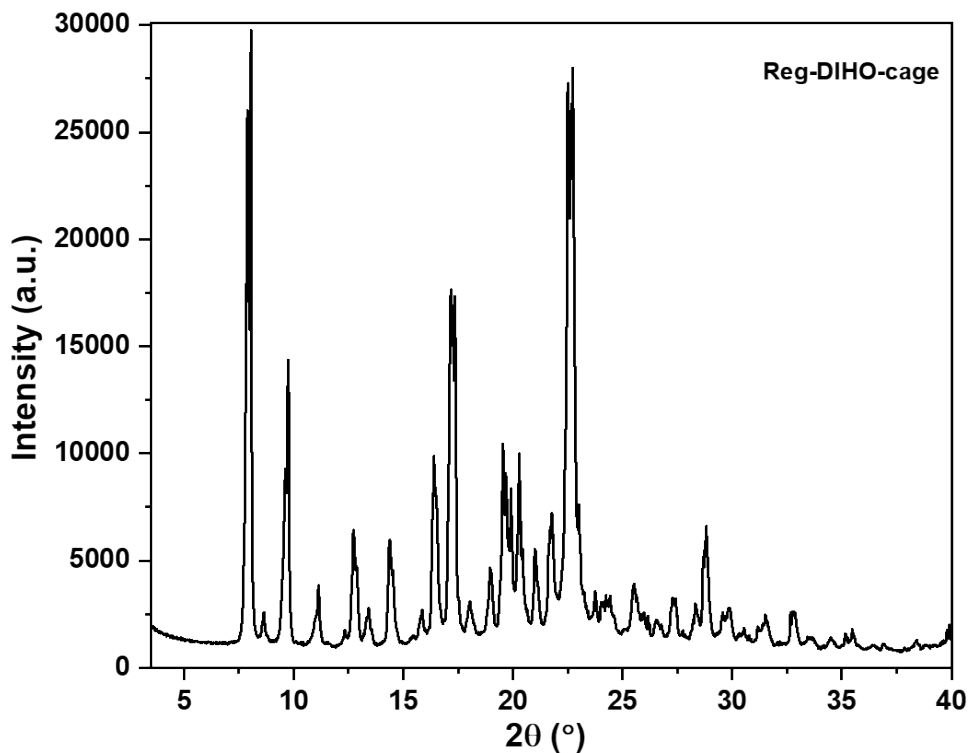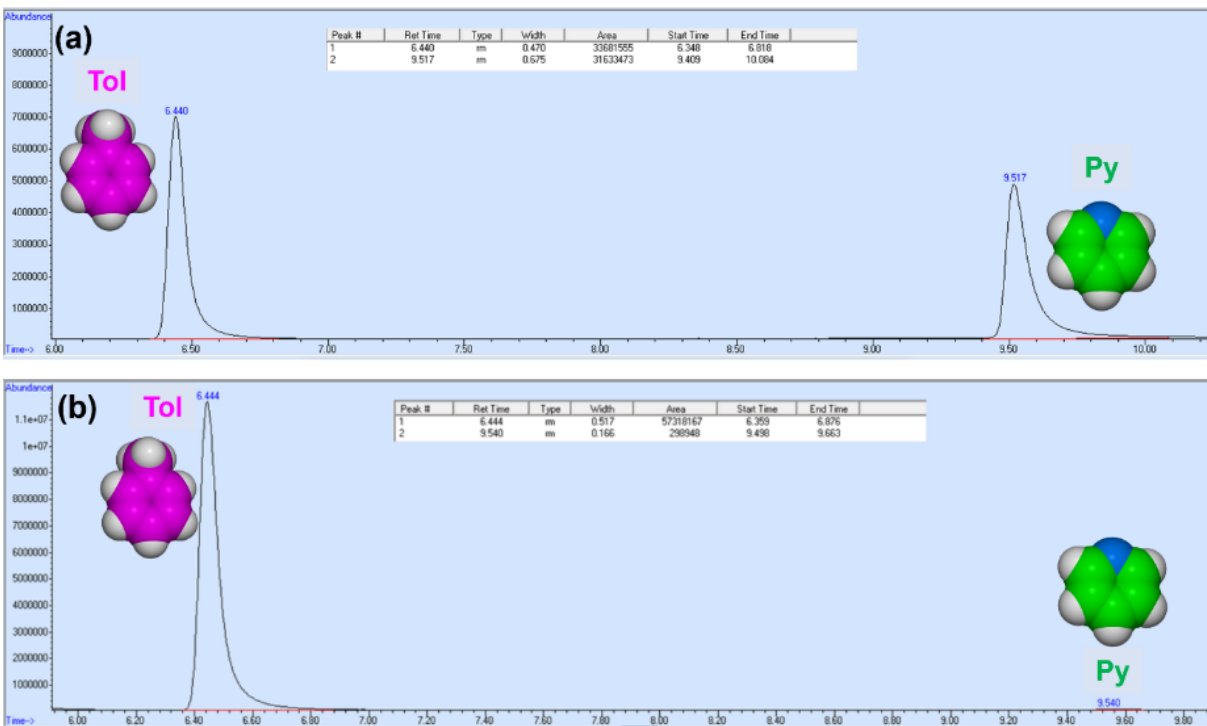
Table S1: Crystallographic details of **DIHO-cage** in different solvents.

IDENTIFICATION CODE	DIHO-cage@CHCl$_3$	DIHO-cage@DCM	DIHO-cage@Py	DIHO-cage@Tol	DIHO-cage@Tol/Py
Empirical formula	C$_{38}$H$_{44}$Cl$_6$N$_8$O$_6$	C$_{38}$H$_{46}$Cl$_4$N$_8$O$_6$	C$_{36}$H$_{42}$N$_8$O$_6$	C$_{43}$H$_{50}$N$_8$O$_6$	C$_{43}$H$_{50}$N$_8$O$_6$
Formula weight (g/mol)	921	852.63	682.77	774.91	774.92
Temperature /K	120	120.0	150	120	120
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2$_1$/c	P2$_1$/n	P2$_1$/c	P2$_1$/c
a/ Å	19.3748(3)	16.3524(5)	13.685(4)	13.658(3)	13.5377(7)
b/ Å	14.5735(2)	14.3350(4)	16.419(4)	9.8012(18)	9.7771(5)
c/ Å	16.4860(2)	18.8597(5)	15.856(4)	30.782(5)	30.4812(15)
α/°	90	90	90	90	90
β/°	115.7580(10)	113.765(2)	102.268(8)	99.251(12)	99.479(2)
γ/°	90	90	90	90	90
Volume/ Å^3	4192.43(11)	4046.1(2)	3481.4(16)	4067.0(13)	3979.4(3)
Z	4	4	4	4	4
ρcalcg/cm^3	1.460	1.400	1.303	1.266	1.293
F(000)	1912	1784	1448	1648	1653
Crystal size/mm^{-3}	0.1 x 0.2 x 0.3	0.1 x 0.2 x 0.3	0.1 x 0.2 x 0.3	0.1 x 0.2 x 0.3	0.1 x 0.2 x 0.3
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	GaKα (λ = 1.34139)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
reflections collected	29392	82129	85187	36177	72943
Independent reflections	3687(R_{int} = 0.0651)	7412(R_{int} = 0.0674)	8602 (R_{int} = 0.0838)	6639(R_{int} = 0.0905)	7014(R_{int} = 0.0428)
Data/restraints/parameters	2965/0/274	5864/0/529	7370/0/475	3527/0/522	7014/0/539
Goodness-of-fit on F2	1.024	0.982	1.076	0.997	1.059
Final R indexes [I>=2σ (I)]	R1 = 0.0406, wR2 = 0.1014	R1 = 0.0511, wR2 = 0.1411	R1 = 0.0447, wR2 = 0.1212	R1 = 0.0547, wR2 = 0.1395	R1 = 0.0343, wR2 = 0.0860
CCDC	2361427	2361428	2361429	2361430	2361431

Table S2: Some important host/guest hydrogen bonding intermolecular interactions between **DIHO-cage** and **Tol** in **DIHO-cage@Tol** crystal structure.

Distance	D···A (Å)	H···A (Å)	>D–H···A (°)
C11–H11B···*i*1	3.703	2.799	152.25
C25–H25A···*i*1	3.882	2.904	169.89
C39–H39···O5	3.434	2.810	124.10
C40–H40···O2	3.767	2.860	160.15
C41–H41···O4	3.756	3.043	133.03
C43–H43C···O3	3.497	2.566	158.48

Table S3: Some important host/host hydrogen bonding intermolecular interactions between **DIHO-cages** in **DIHO-cage@Tol** crystal structure.

Distance	D···A (Å)	H···A (Å)	>D–H···A (°)
C14–H14···O3	3.397	2.487	160.41
C22–H22···O1	3.383	2.441	171.29
C56–H56···N2	3.487	3.074	107.98

References

1. Z. Cai, J. Du, T. Huang, Y. Ding and M. Wu, *CrystEngComm*, 2023, **25**, 5778–5781.

2. SAINT. Bruker AXS. Inc, Madison, Wisconsin, USA, 2014.

3. G. M. Sheldrick, SADABS. University of Gottingen, Germany, 2008.

4. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.

5. L. J. Barbour, *Supramol. Chem.* 2001, **1**,189 –191.

6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.