

**Supporting Information**  
**Highly selective molecular sieving of cis- over trans-1,2-**  
**dichloroethene isomers**

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## 1. Materials

All chemicals and solvents were purchased from commercial supplies and used without further purification.

## 2. Instrument and characterization

### Nuclear magnetic resonance (NMR)

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained on Bruker 400 MHz or 500 MHz spectrometers. Chemical shifts were reported in ppm relative to the residual solvent peak ( $\text{CDCl}_3$ :  $^1\text{H}$ , 7.26;  $^{13}\text{C}$ , 77.23).

### Thermogravimetric analysis (TGA)

TGA was carried out using an automatic sample loading TA instrument Q5000 analyzer. The samples were heated at the rate of 10 °C/min using  $\text{N}_2$  as the protective gas.

### Single crystal X-ray diffraction (SCXRD)

SCXRD intensity data were collected using a Bruker D8 Venture with Photon II CPAD diffractometer (Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) equipped with Incoatec  $\text{I}\mu\text{S}$  microfocus source, multilayer monochromator for the crystal structure. The crystal was collected at 120 K supported by Oxford Cryosystems 800 Plus cryostat. Data reductions were carried out by means of a standard procedure using the Bruker software package SAINT.<sup>S1</sup> The absorption corrections and the correction of other systematic errors were performed using SADABS.<sup>S2</sup> The structures were solved by direct methods using SHELXS-2008 and refined using SHELXL-2018.<sup>S3</sup> X-Seed<sup>S4</sup> was used as the graphical interface for the SHELX program suite. For all the cases non-hydrogen atoms were refined anisotropically. All other hydrogen atoms are geometrically fixed using riding atom model.

### **Powder X-ray diffraction (PXRD)**

PXRD data was obtained at room temperature on a Bruker D8 ADVANCE X-ray diffractometer (40 kV, 40 mA) with the Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Data was measured over the range of 5-40° in 5°/min steps.

### **Gas chromatographic (GC)**

GC measurements were carried out using an Agilent 7890A instrument configured with an FID detector and a DB-624 column (60 m  $\times$  0.25 mm  $\times$  1.4  $\mu$ m). The following GC method was used: the oven was programmed from 30 °C with a 2 min hold, ramped in 5 °C/min increments to 100 °C with 2 min hold and further ramped 25 °C/min increments to 150 °C. The total run time was 20 min and the injection temperature was 250 °C. Detection was performed using a single-quadrupole mass spectrometry in EI positive mode with a mass range of 35-300 m/z. The helium (carrier gas) flow rate was 1.0 mL/min. The samples were injected in the split mode (20:1).

### **Single crystal growth**

Single crystals of **1A** were obtained by the slow diffusion of methanol into a dichloromethane solution at room temperature. Single crystals of *cis*-DCE@**1** were obtained by the slow diffusion of methanol into a *cis*-DCE solution at room temperature. Single crystals of *trans*-DCE@**1** were obtained by the slow diffusion of methanol into a *trans*-DCE solution at room temperature.

### **Competitive crystallization**

Macrocyclic **1** was dissolved in an equimolar mixture of *cis*- and *trans*-DCE, then single crystals were obtained by vapor diffusion of methanol into the above solution at room temperature.

### **Adsorption material activation**

Single crystals of **1A** were dried under vacuum at 80 °C for 24 h to obtain the activated adsorptive materials (**1 $\alpha$** ). The **1 $\alpha$**  after adsorption could be regenerated to release the adsorbed guests upon heating at 100 °C under vacuum overnight.

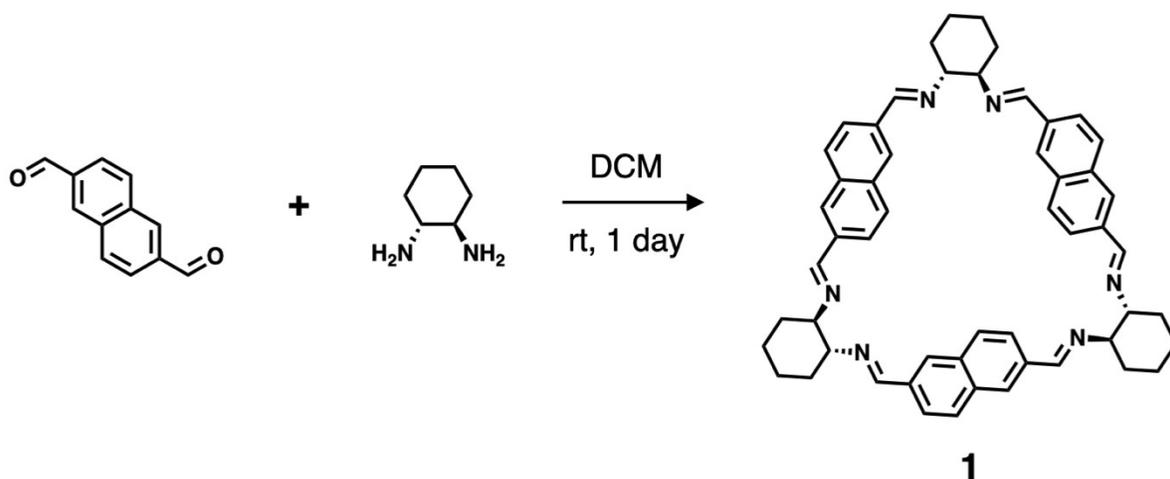
### **Adsorption experiments for *cis*- or *trans*- DCE vapor.**

An open 5 mL vial containing 20 mg of the **1 $\alpha$**  adsorbent was placed in a sealed 20 mL vial containing 1 mL of solvents (*trans*-DCE, *cis*-DCE, or an equimolar *cis/trans*-DCE mixture). The uptake capacity of **1 $\alpha$**  was measured at different time intervals by <sup>1</sup>H-NMR.

### **N<sub>2</sub> and CO<sub>2</sub> adsorption.**

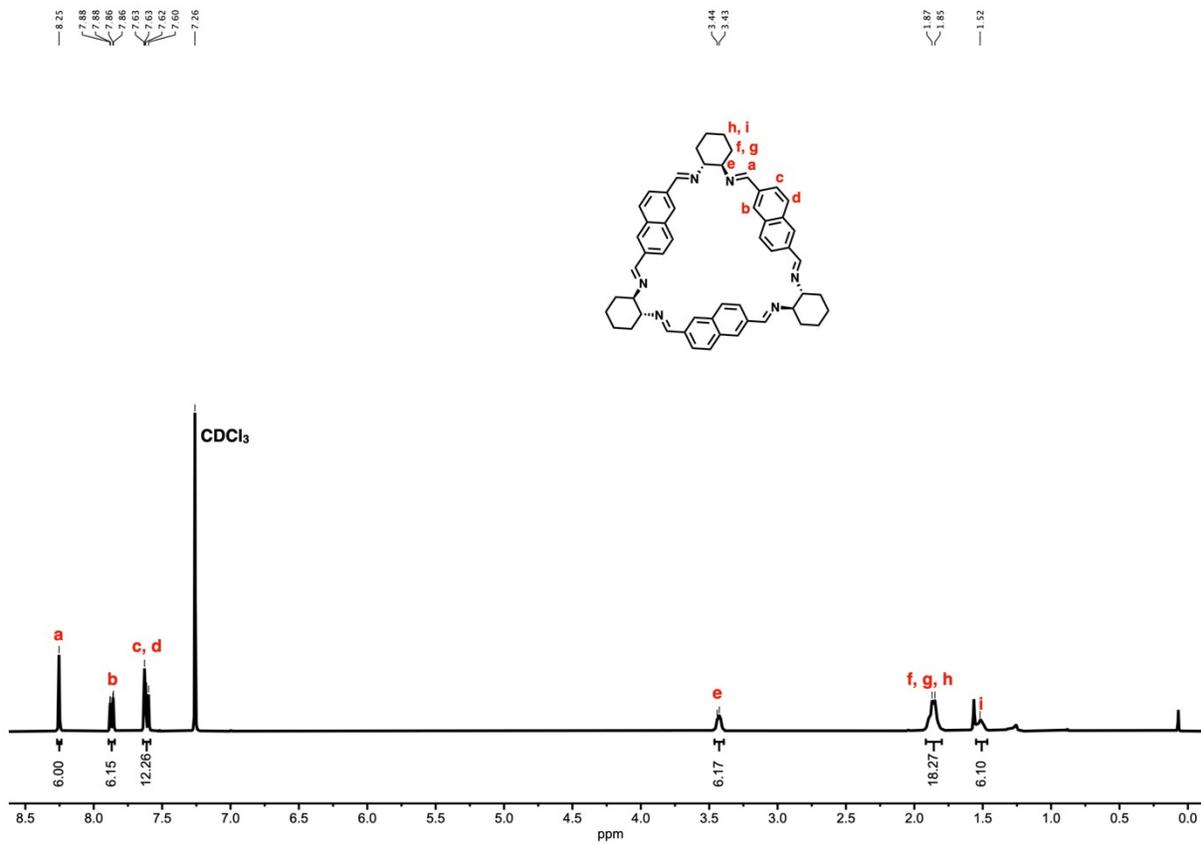
Low-pressure gas adsorption measurement was performed on a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP) 2020 surface area analyzer. Samples were degassed under dynamic vacuum over night at 150 °C prior to each measurement. N<sub>2</sub> and CO<sub>2</sub> isotherms were measured using a liquid nitrogen (77 K) and water (298 K) baths respectively.

## Synthesis of trianglimine **1**.

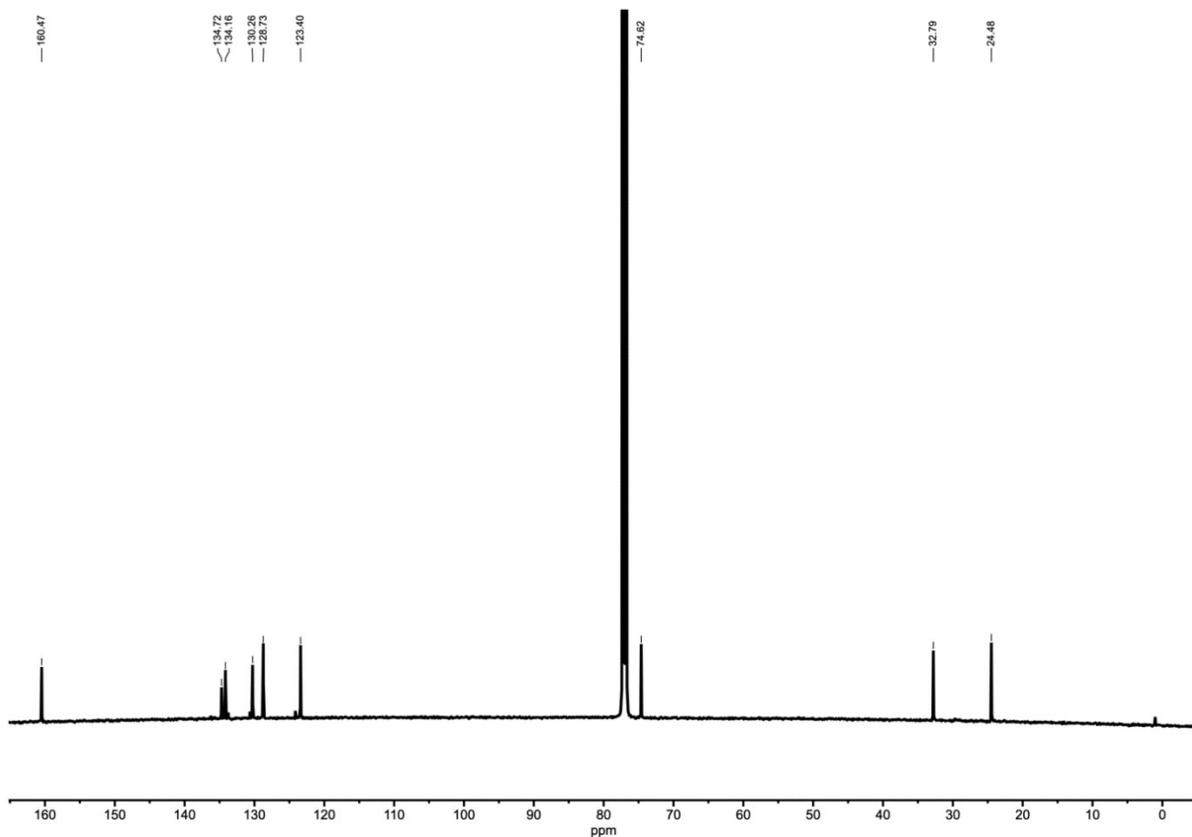


### Scheme S1. Synthetic scheme of macrocycle **1**.

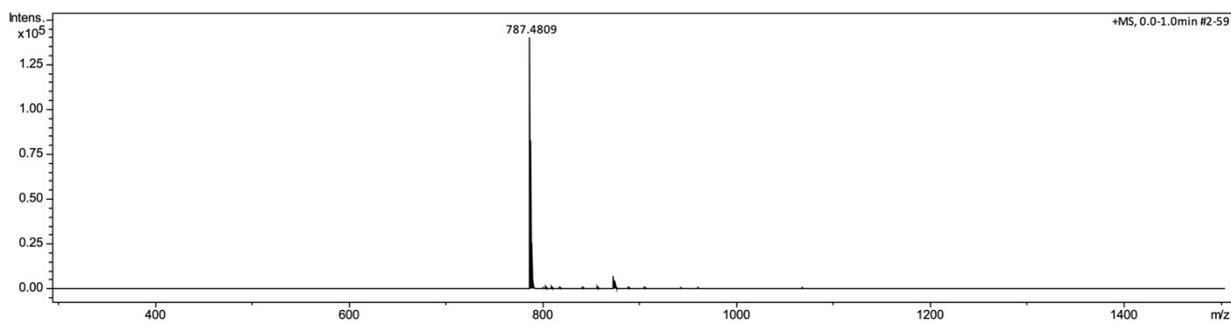
A mixture of (1R, 2R)-diaminocyclohexane (296 mg, 2.6 mmol) and naphthalene-2,6-dicarbaldehyde (480 mg, 2.6 mmol) in dichloromethane (80 mL) was stirred at room temperature for 24 h. The white precipitate was isolated by filtration and washed with methanol. The product was dried by vacuum to provide 91% (621 mg) yield of white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 7.97 – 7.82 (m, 1H), 7.76 – 7.55 (m, 2H), 3.54 – 3.35 (m, 1H), 1.99 – 1.77 (m, 3H), 1.59 – 1.46 (m, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.47, 134.72, 134.16, 130.26, 128.73, 123.40, 74.62, 32.79, 24.48. HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{54}\text{H}_{55}\text{N}_6$ : 787.45; found 787.48.



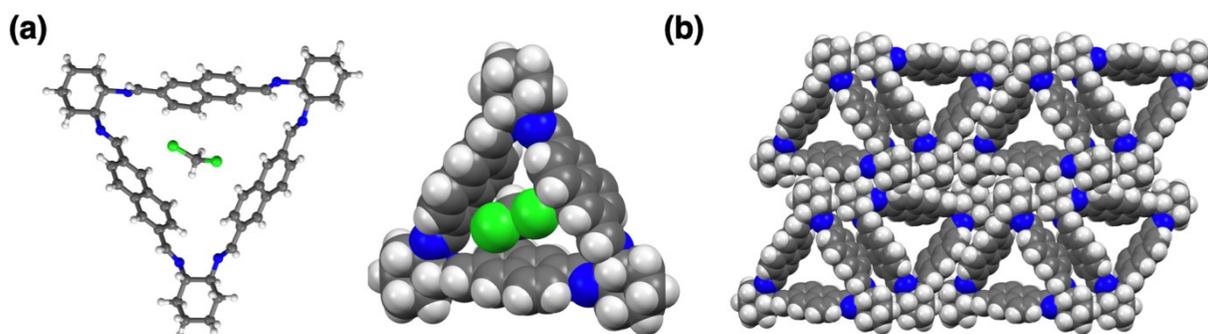
**Figure S1.** <sup>1</sup>H NMR spectrum of **1**.



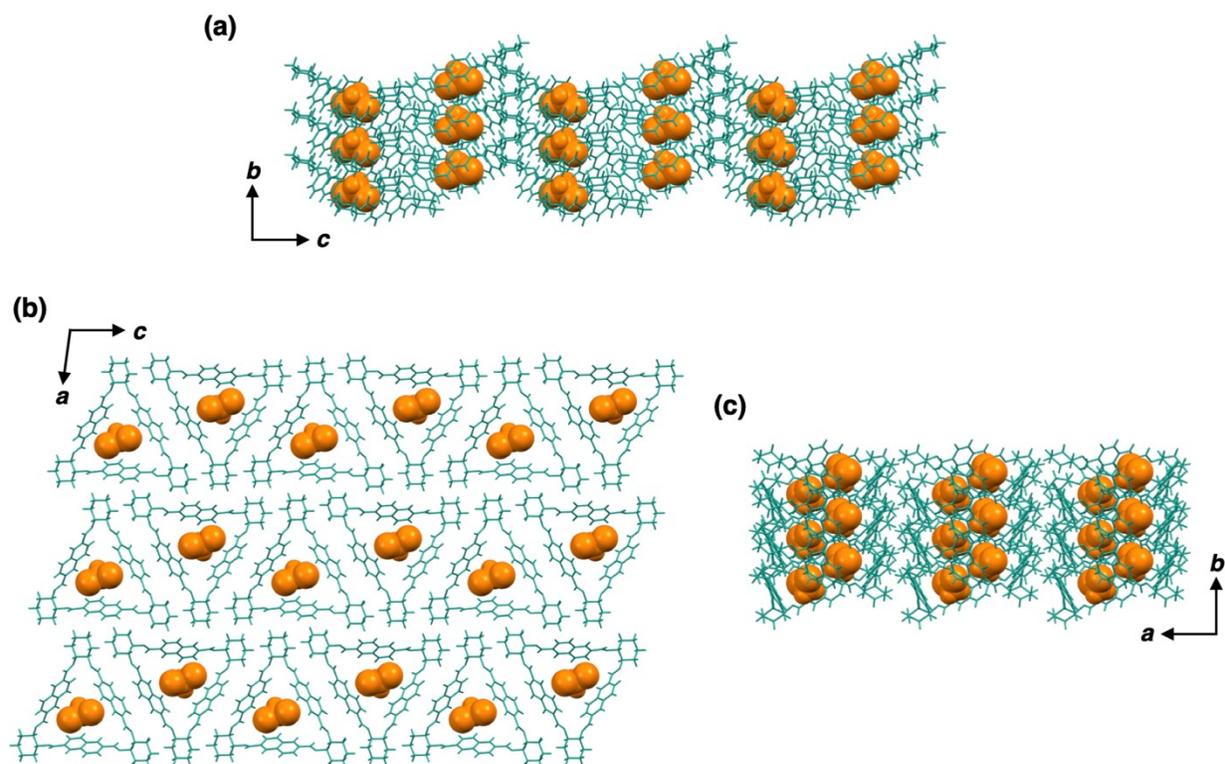
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of **1**.



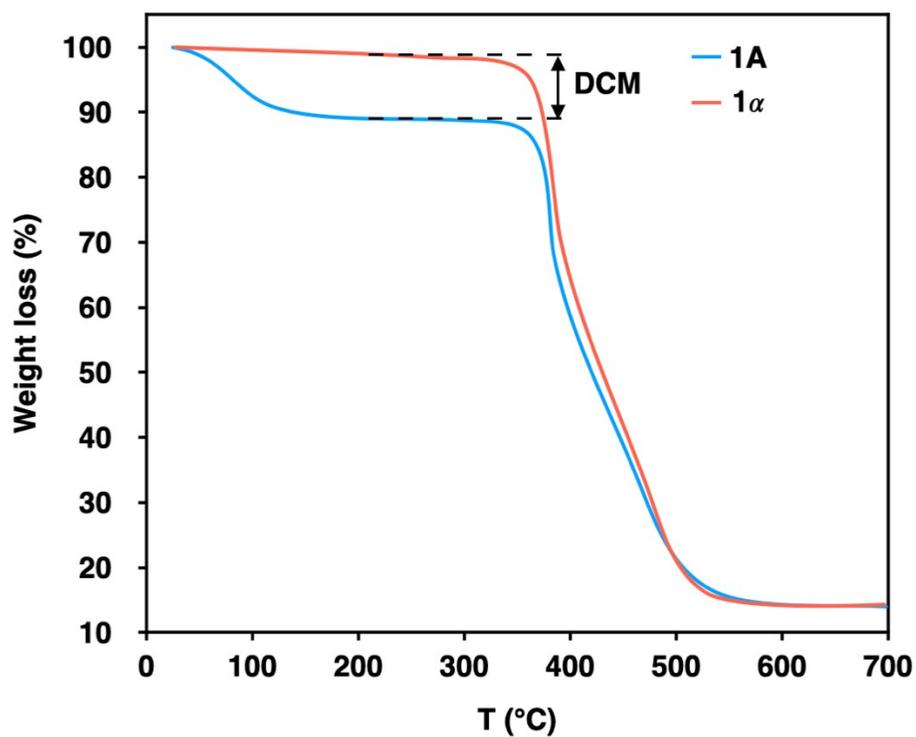
**Figure S3.** HRMS:  $m/z$   $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{54}\text{H}_{55}\text{N}_6$ : 787.45; found 787.48 for macrocycle **1**.



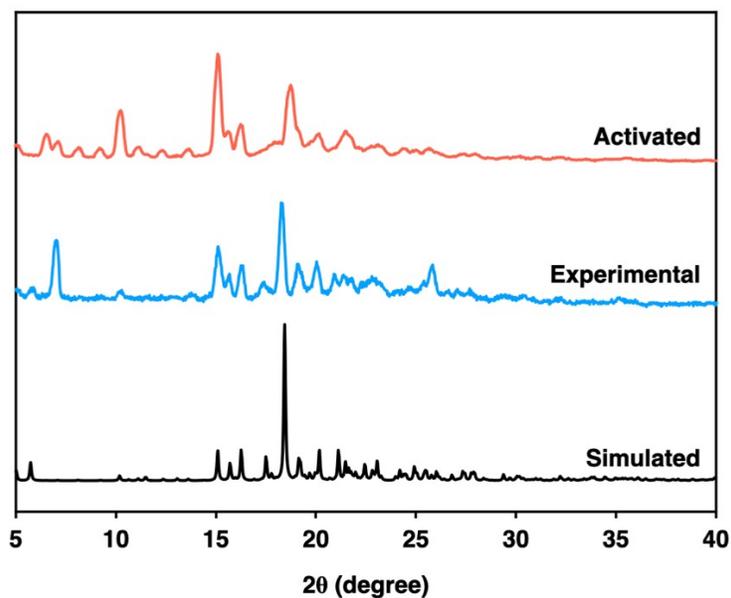
**Figure S4.** (a) The asymmetric unit and its space filling structure for crystalline **1A**. (b) Crystalline **1A** assembled in a head-tail fashion that generates a layered structure with connecting channels.



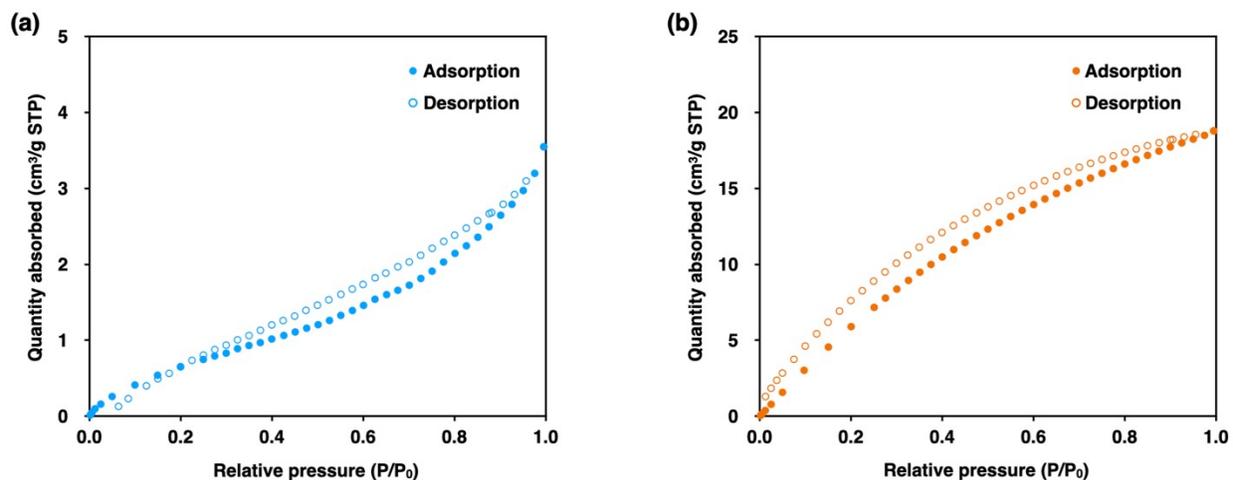
**Figure S5.** Packing arrangement of crystal **1A** along (a) *a*-axis (b) *b*-axis (c) *c*-axis.



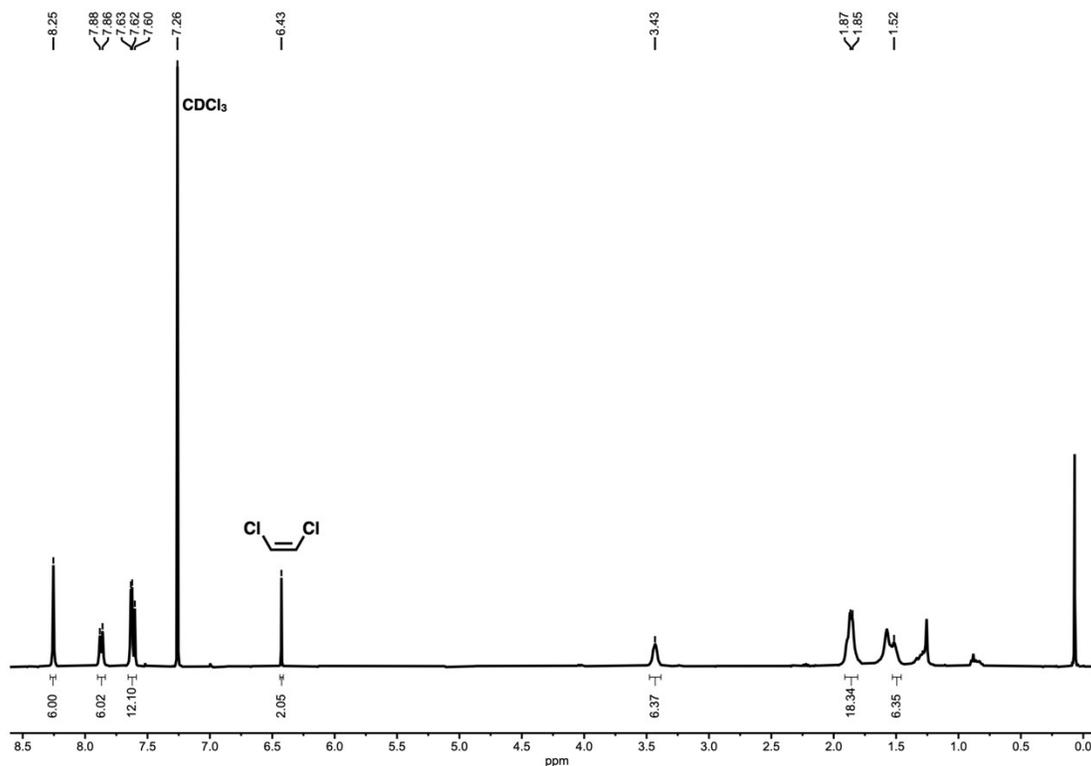
**Figure S6.** TGA curves of the crystalline **1A** and activated one **1α**.



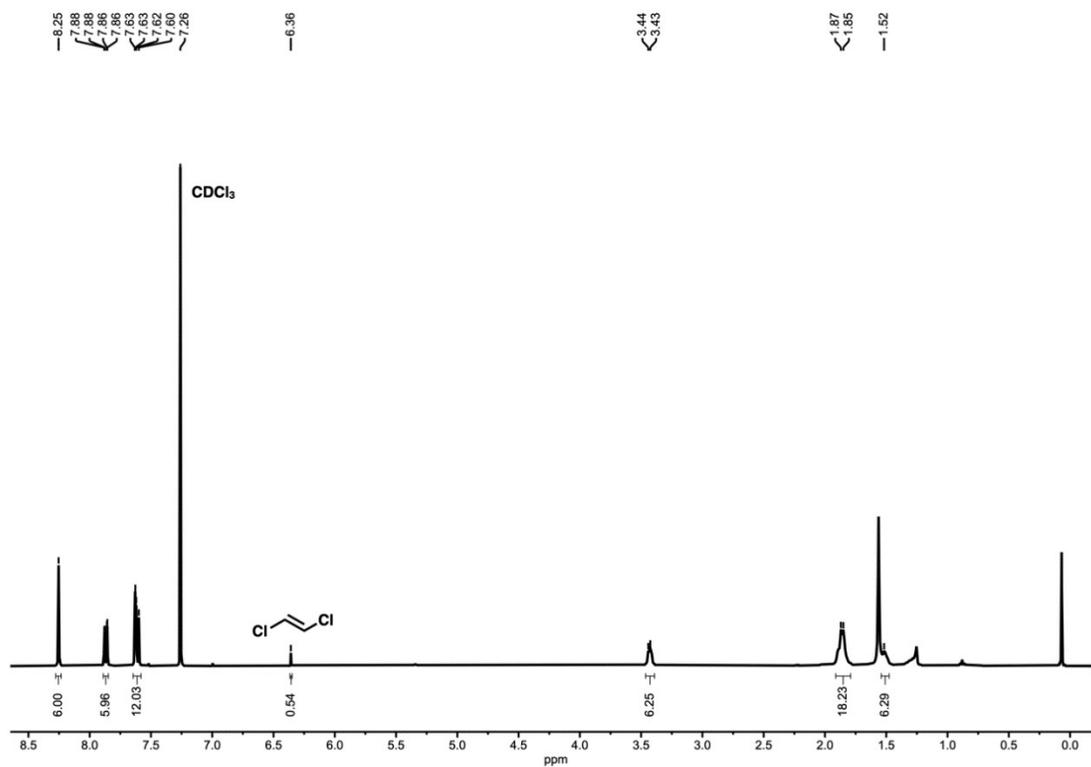
**Figure S7.** The PXRD patterns of the crystalline **1A**, **1α** and the corresponding simulated patterns.



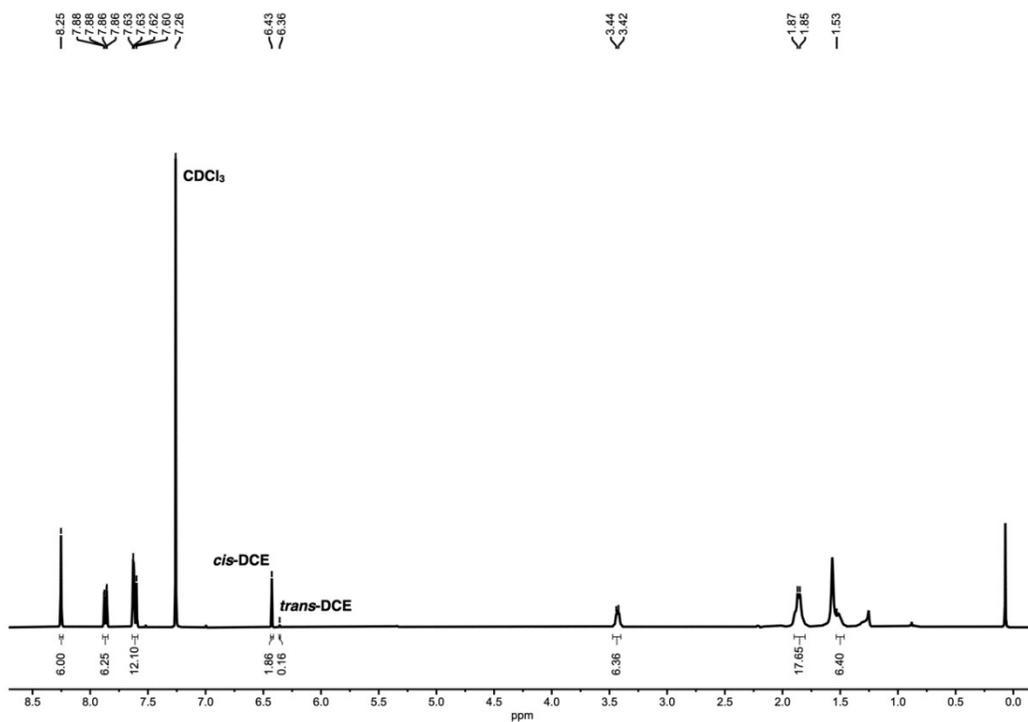
**Figure S8.** Isotherms showing (a) N<sub>2</sub> gas adsorption of **1α** at 77 K and (b) CO<sub>2</sub> gas adsorption of **1α** at 298 K.



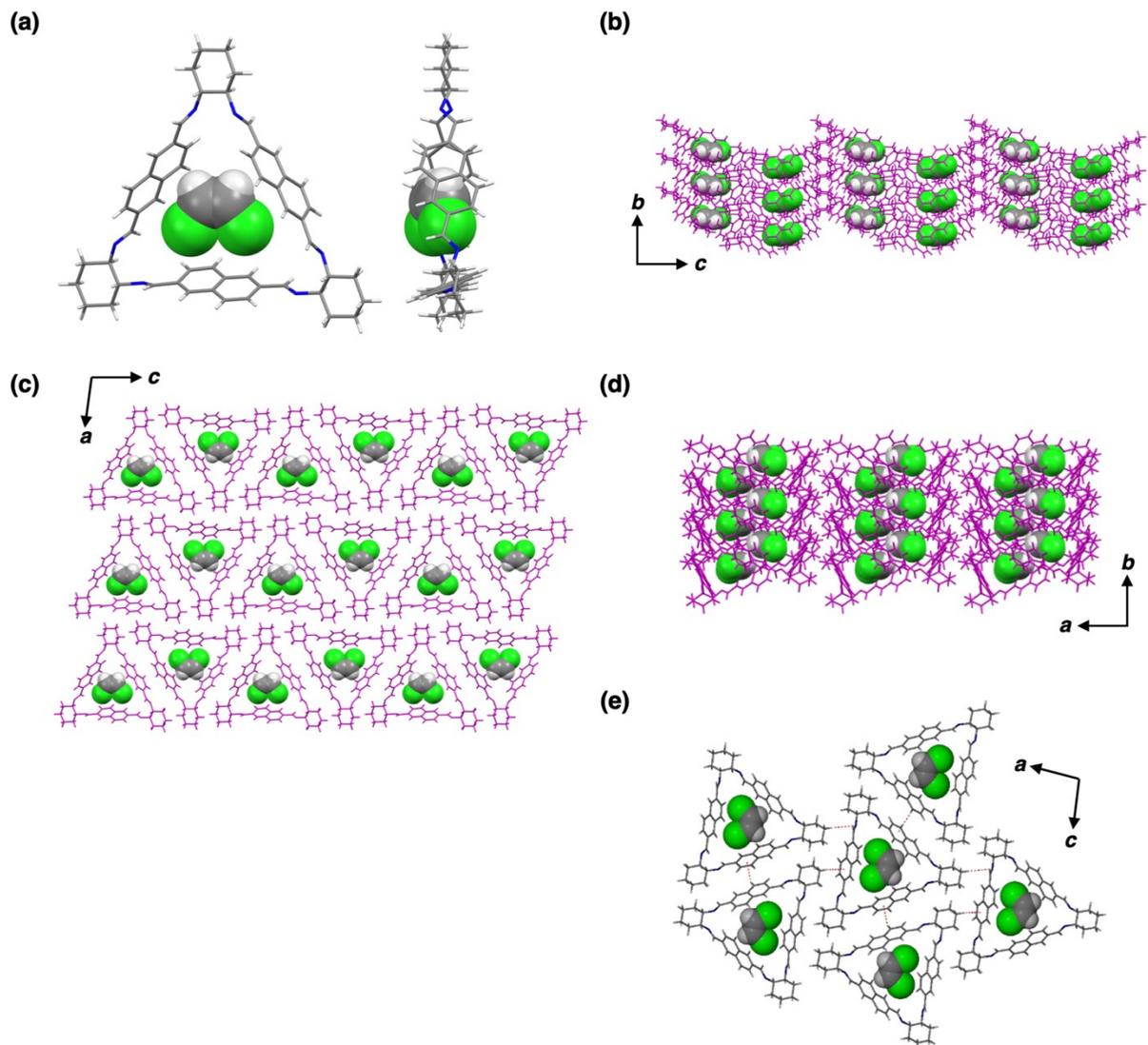
**Figure S9.** <sup>1</sup>H NMR spectrum of **1α** after being exposed to *cis*-DCE for 1 h.



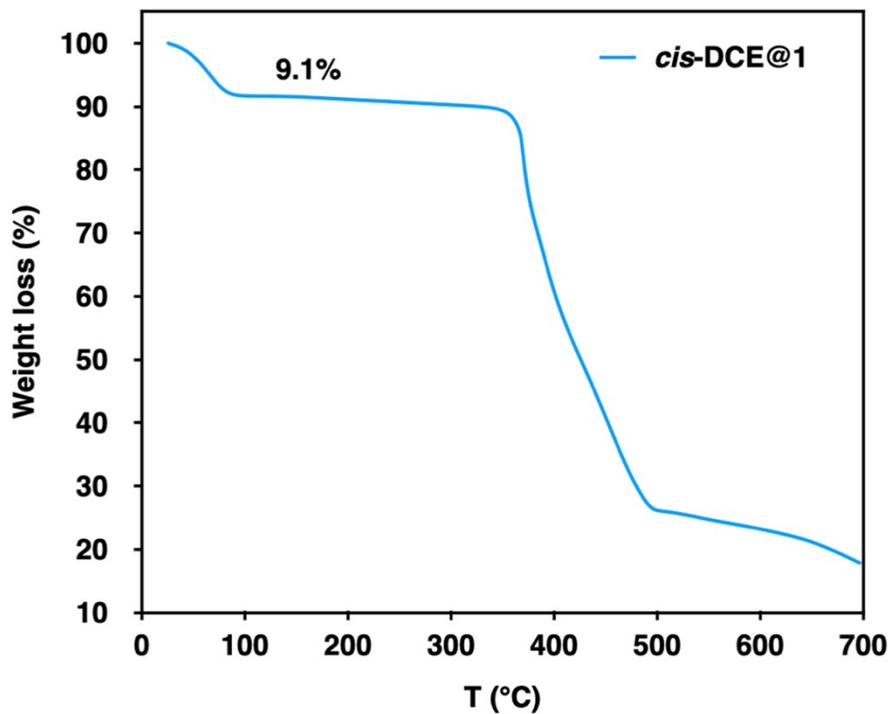
**Figure S10.**  $^1\text{H}$  NMR spectrum of  $1\alpha$  after being exposed to *trans*-DCE for 1 h.



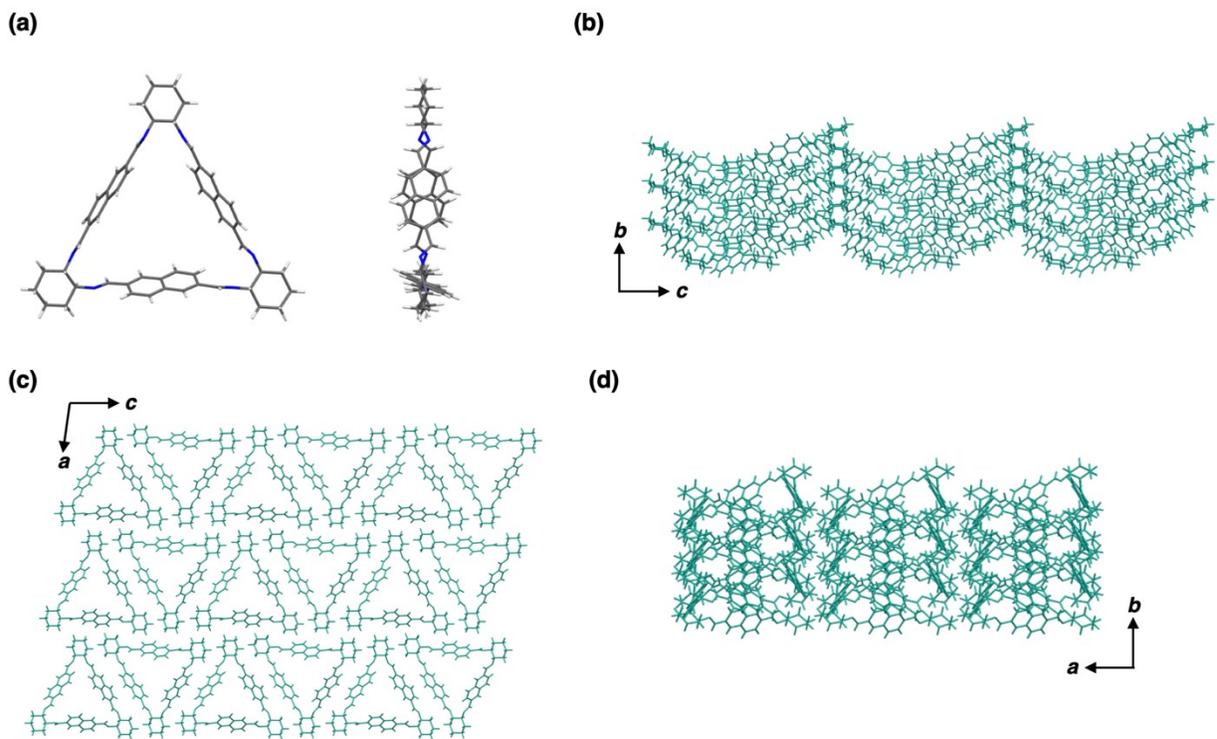
**Figure S11.**  $^1\text{H}$  NMR spectrum of  $1\alpha$  after being exposed to equimolar *cis/trans*-DCE for 1 h.



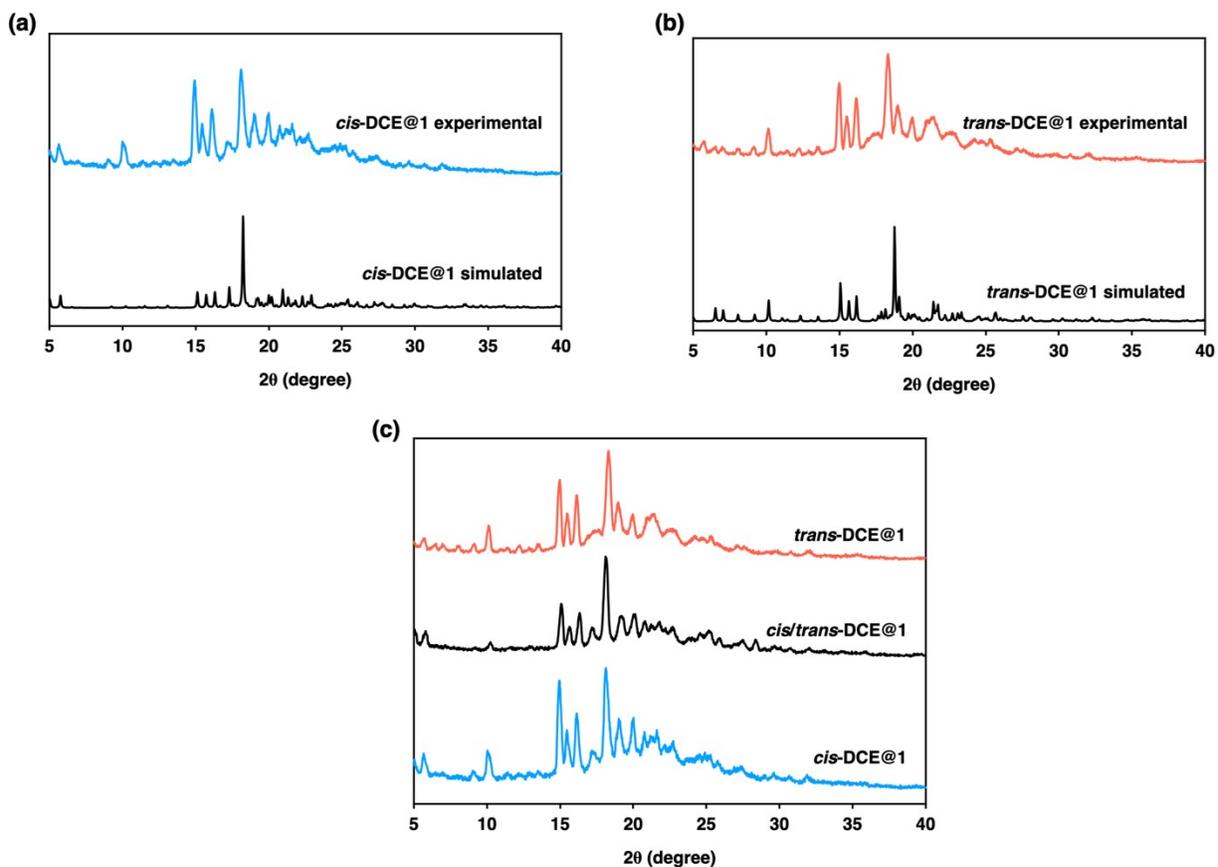
**Figure S12.** (a) Crystal structure of *cis*-DCE@1. Packing arrangement of crystal *cis*-DCE@1 along (b) *a*-axis (c) *b*-axis (d) *c*-axis and (e) showing host/host intermolecular interactions along *b*-axis.



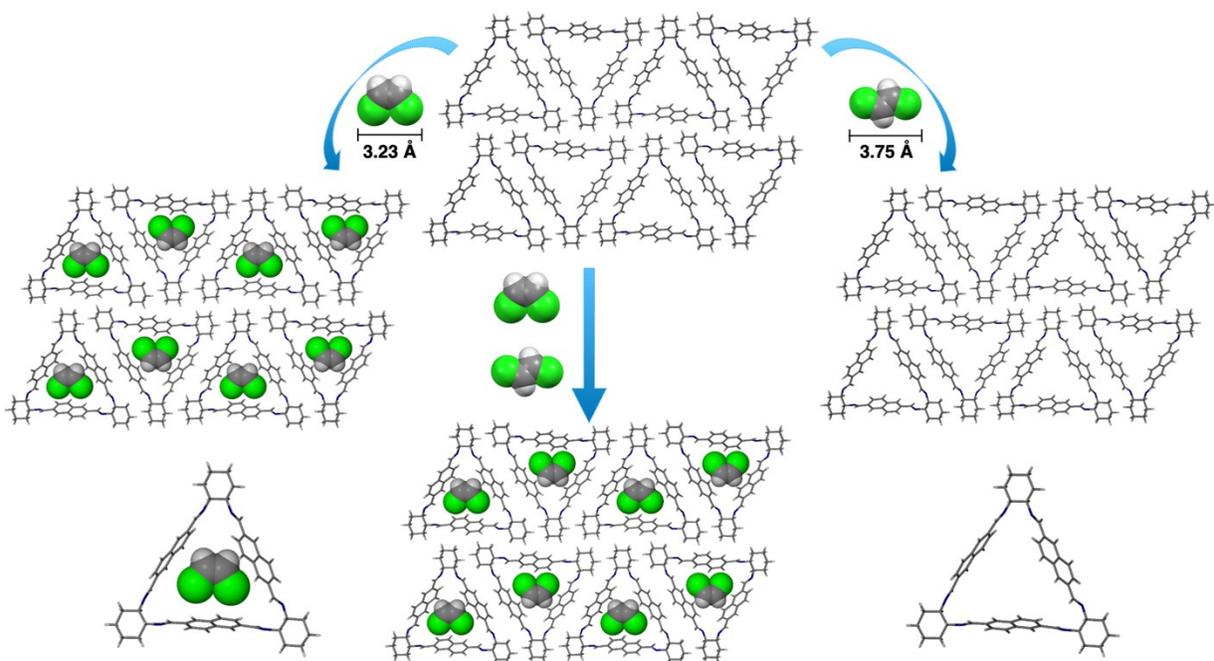
**Figure S13.** TGA curve of *cis*-DCE@1 crystal.



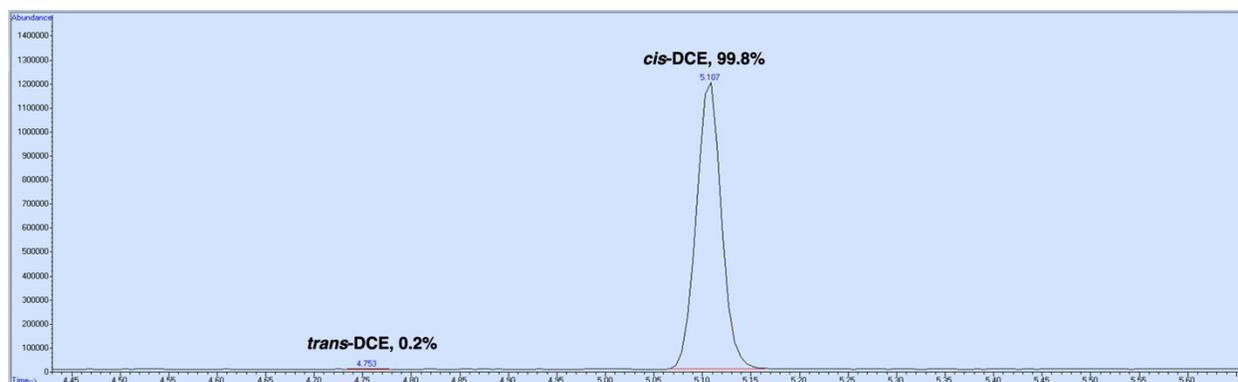
**Figure S14.** (a) Crystal structure of *trans*-DCE@1. Packing arrangement of the crystal structure along (b) *a*-axis (c) *b*-axis (d) *c*-axis.



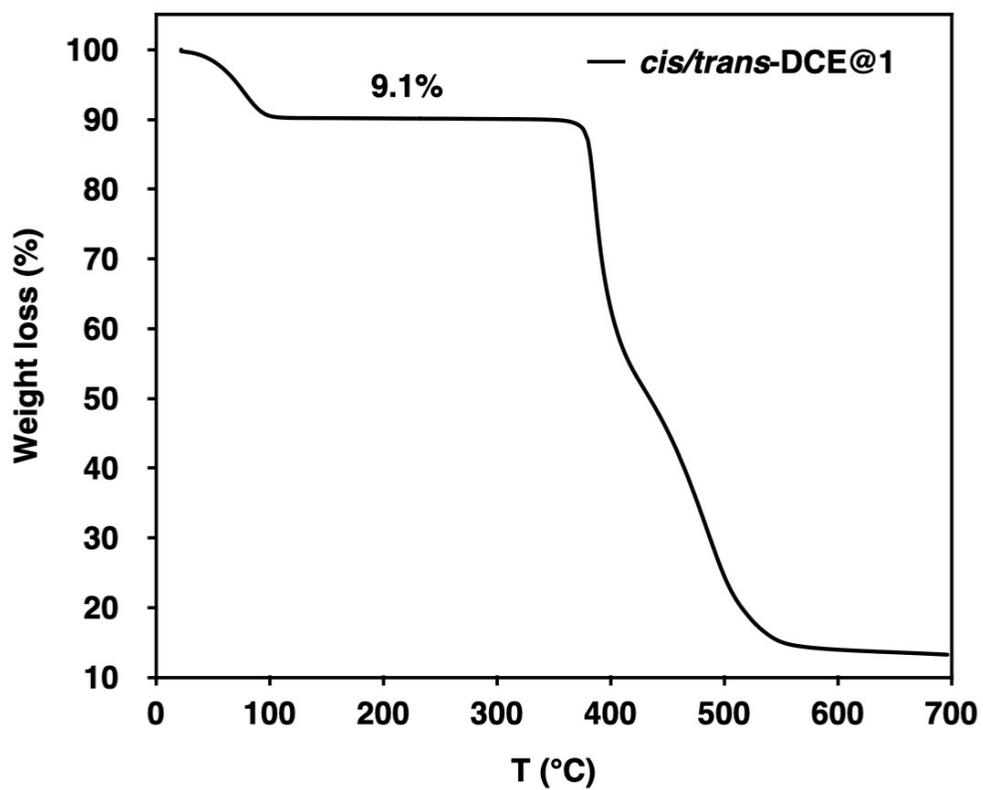
**Figure S15.** Comparison of simulated and experimental PXRD patterns of (a) *cis*-DCE@1. (b) *trans*-DCE@1. (c) *trans*-DCE@1, *cis*-DCE@1 and *cis/trans*-DCE@1.



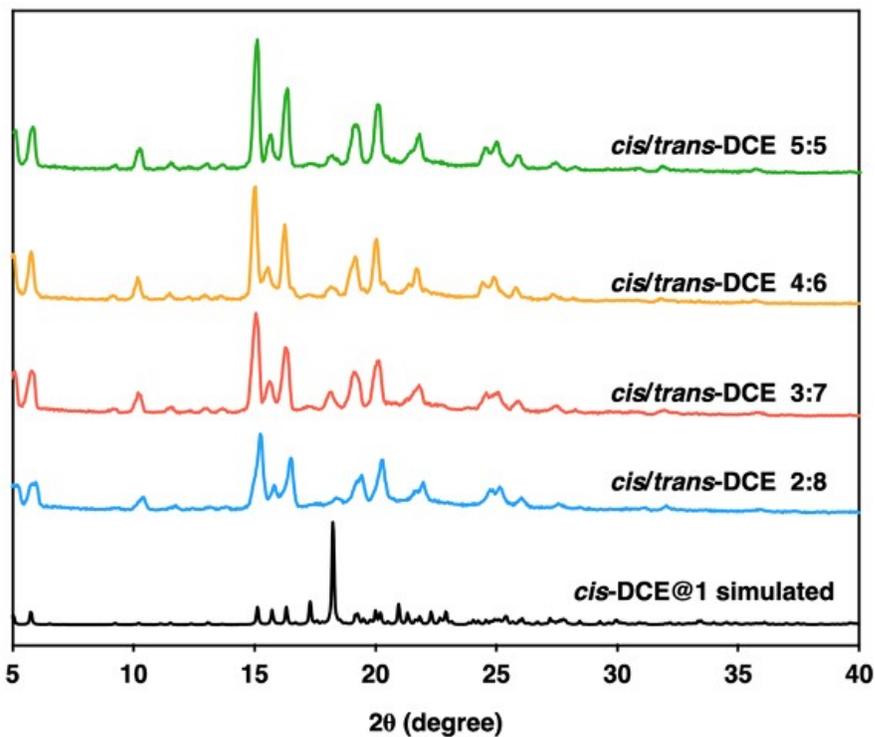
**Figure S16.** Schematic presentation of the selectivity of macrocycle **1** towards *cis*- over *trans*-DCE.



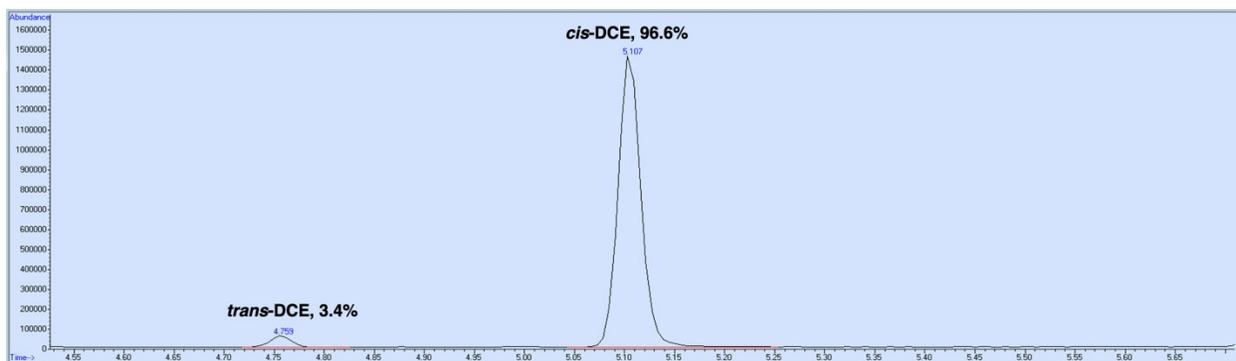
**Figure S17.** GC shows the relative amount of *cis*- and *trans*-DCE in crystal form competitive crystallization.



**Figure S18.** TGA curve of *cis/trans*-DCE@1.



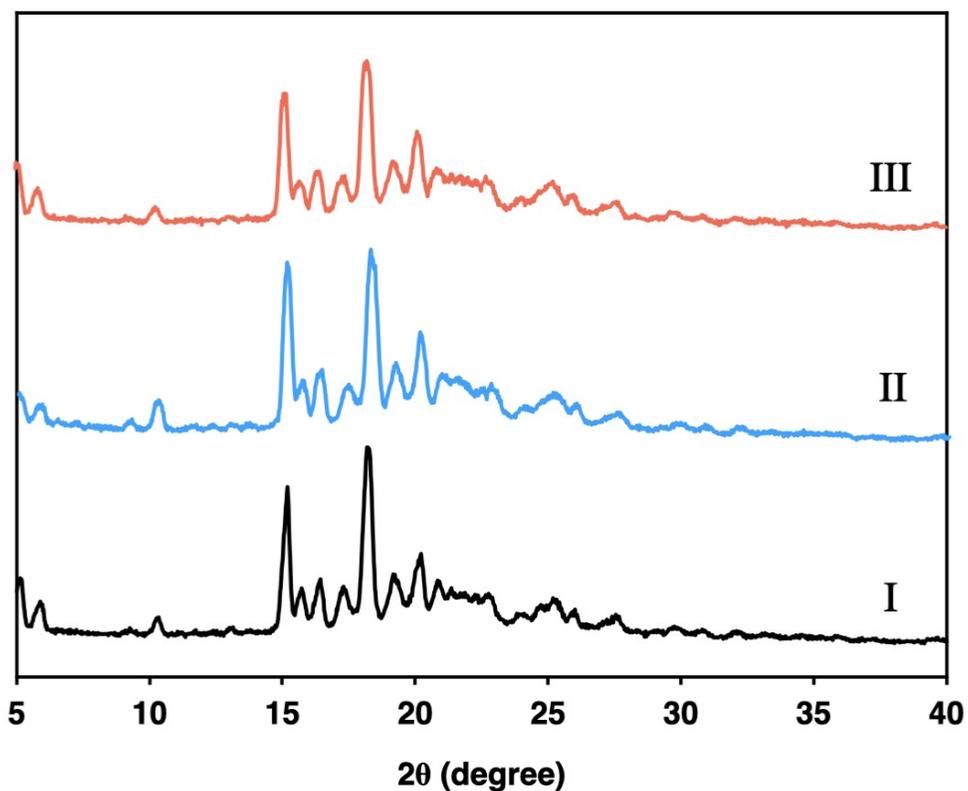
**Figure S19.** PXRD patterns of  $1\alpha$  after sorption of different fractions of *cis/trans*-DCE mixtures for 1 h at 298K.



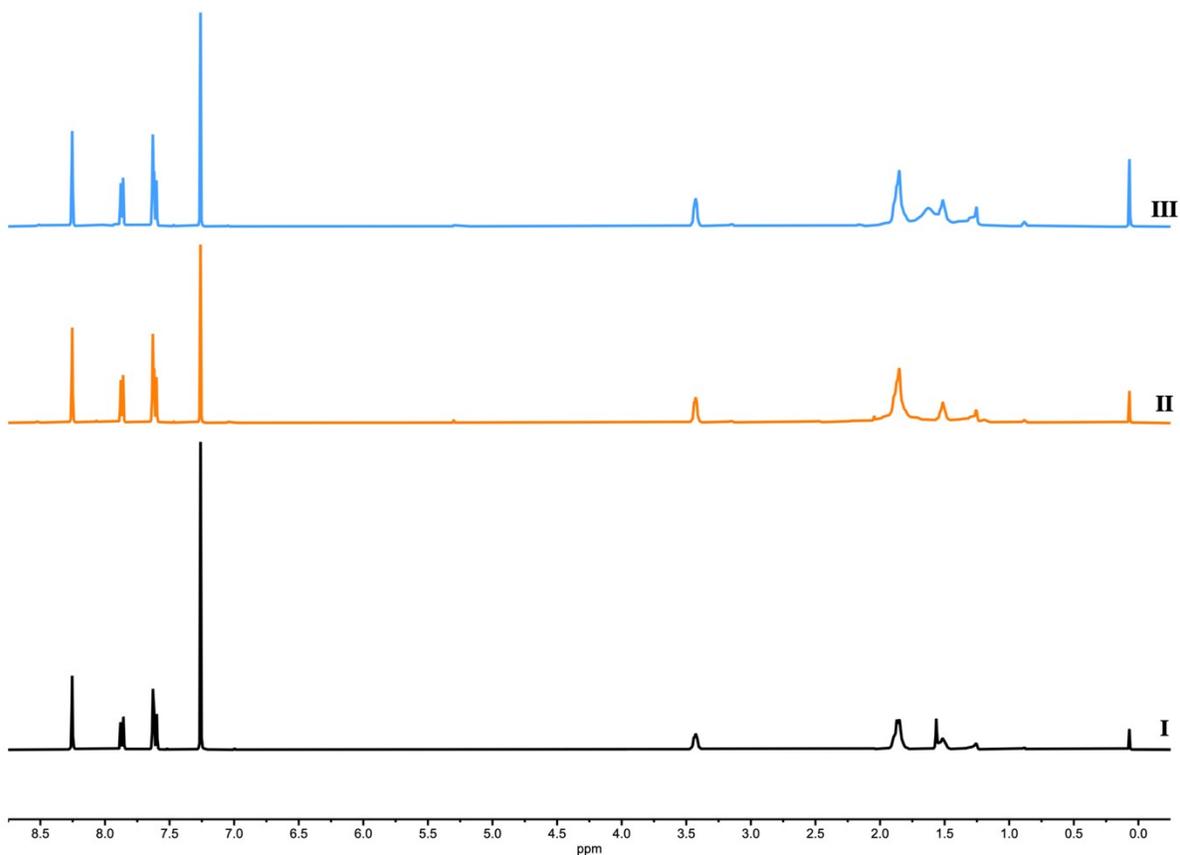
**Figure S20.** GC shows the relative amount of *cis*- and *trans*-DCE adsorbed by  $1\alpha$  from *cis/trans*-DCE mixture for 1 h.



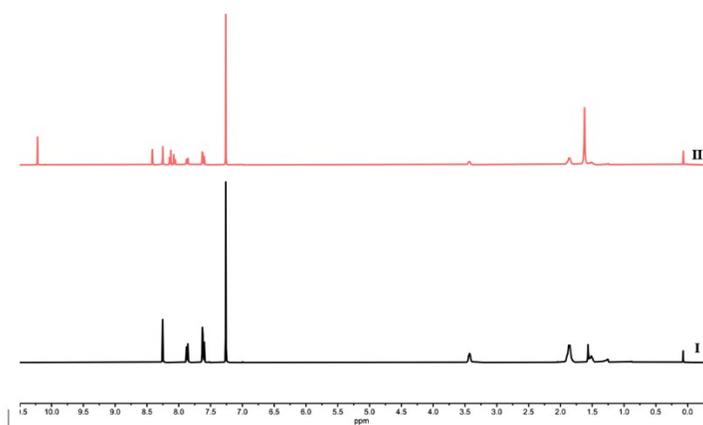
**Figure S21.** Optical images of  $1\alpha$  as a selective absorbent for *cis/trans*-DCE from vapor and liquid isomeric mixtures.



**Figure S22.** Experimental PXRD patterns of  $1\alpha$  after being exposed to a *cis/trans*-DCE mixture for 1 h.  $1\alpha$  was regenerated at 100 °C under vacuum for each cycle. (I) first cycle. (II) third cycle. (III) fifth cycle.



**Figure S23.**  $^1\text{H}$  NMR spectra showing the stability of macrocycle **1** (I) original (II) in water and (III) 1M NaOH for 5 days.



**Figure S24.**  $^1\text{H}$  NMR spectra showing the stability of macrocycle **1** (I) original (II) in 0.1 M HCl.

**Table S1.** Experimental single crystal X-ray data.

| IDENTIFICATION CODE                | 1A   | <i>cis</i> -DCE@1  | <i>trans</i> -DCE@1                            | <i>cis/trans</i> -DCE@1  |
|------------------------------------|--|--|--|--|
| Empirical formula                  | C <sub>55</sub> H <sub>56</sub> Cl <sub>2</sub> N <sub>6</sub> | C <sub>56</sub> H <sub>56</sub> Cl <sub>2</sub> N <sub>6</sub> | C <sub>55</sub> H <sub>54</sub> N <sub>6</sub> | C <sub>56</sub> H <sub>56</sub> Cl <sub>2</sub> N <sub>6</sub> |
| Formula weight (g/mol)             | 871.95   | 883.96   | 799.04   | 883.96   |
| Temperature /K                     | 120  | 120.0  | 120.0  | 120.0  |
| Crystal system                     | Monoclinic   | Monoclinic   | Monoclinic                                     | Monoclinic   |
| Space group                        | P2 <sub>1</sub>  | P2 <sub>1</sub>  | P2 <sub>1</sub>                                | P2 <sub>1</sub>  |
| a/ Å                               | 17.7583(19)  | 17.7194(16)  | 17.796(3)                                      | 17.7147(11)  |
| b/ Å                               | 5.3589(6)  | 5.4334(5)  | 5.2354(7)                                      | 5.4402(3)  |
| c/ Å                               | 25.148(3)  | 25.100(2)  | 25.302(4)                                      | 25.1280(15)  |
| α/°                                | 90   | 90   | 90   | 90   |
| β/°                                | 97.803(4)  | 97.674(4)  | 98.005(5)                                      | 97.604(3)  |
| γ/°                                | 90   | 90   | 90   | 90   |
| Volume/ Å <sup>3</sup>             | 2371.0(5)  | 2394.9(4)  | 2334.4(6)                                      | 2400.3(2)  |
| Z                                  | 2  | 2  | 2  | 2  |
| ρ <sub>calc</sub> /cm <sup>3</sup> | 1.221  | 1.226  | 1.137  | 1.223  |
| F(000)                             | 924  | 936  | 852  | 936  |
| Radiation                          | MoKα (λ = 0.71073)   | MoKα (λ = 0.71073)   | MoKα (λ = 0.71073)                             | MoKα (λ = 0.71073)   |
| reflections collected              | 42751  | 85085  | 25225  | 37109  |
| Independent reflections            | 11849(R <sub>int</sub> = 0.1788)                               | 9709(R <sub>int</sub> = 0.1193)                                | 11496(R <sub>int</sub> = 0.0629)               | 11884(R <sub>int</sub> = 0.0897)                               |
| Data/restraints/parameters         | 5639/1/568   | 7170/1/577   | 6520/1/546                                     | 7597/1/578   |
| Goodness-of-fit on F <sup>2</sup>  | 1.007  | 1.129  | 1.064  | 1.060  |
| Final R indexes [I >= 2σ(I)]       | R1 = 0.0934, wR2 = 0.1769                                      | R1 = 0.0476, wR2 = 0.1077                                      | R1 = 0.0760, wR2 = 0.1619                      | R1 = 0.0590, wR2 = 0.1191                                      |
| CCDC                               | 2177718  | 2177716  | 2177715  | 2177717  |

**Table S2.** Important intermolecular interactions between host/guest in *cis*-DCE@1.

| Distance            | D···A (Å) | H···A (Å) | >D–H···A (°) |
|---------------------|-----------|-----------|--------------|
| <b>C55–H55···i2</b> | 3.587     | 2.736     | 149.48       |
| <b>C56–H56···i1</b> | 3.563     | 2.763     | 142.48       |

**Table S3.** Important intermolecular hydrogen bonding interactions between host/host in *cis*-DCE@1.

| Distance             | D···A (Å) | H···A (Å) | >D–H···A (°) |
|----------------------|-----------|-----------|--------------|
| <b>C3–H3···i6</b>    | 3.845     | 3.094     | 137.12       |
| <b>C28–H28···i5</b>  | 3.586     | 2.866     | 133.48       |
| <b>C33–H33A···i8</b> | 3.519     | 2.583     | 157.66       |
| <b>C34–H34B···N5</b> | 4.019     | 3.125     | 151.05       |
| <b>C52–H52A···N2</b> | 3.830     | 3.183     | 124.37       |

Symmetry code:

(I) x,y,z Identity Identity 1 1

(II) -x,1/2+y,-z "Screw axis (2-fold)" "2-fold screw axis with direction [0, 1, 0] at 0, y, 0 with screw component [0, 1/2, 0]" 2 2

## References

- (S1) SAINT Data Reduction Software, Version 6.45; Bruker AXS Inc.: Madison, WI, 2003.
- (S2) SADABS, Version 2.05; Bruker AXS Inc.: Madison, WI, 2002.
- (S3) G. M. Sheldrick, A Short History of SHELX. *Acta Crystallogr.* 2008, **A64**, 112 -122.
- (S4) L. J. Barbour, *Supramol. Chem.* 2001, **1**,189 -191.