

Supporting Information

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1. Materials and methods

cis-DCE and *trans*-DCE were purchased from TCI. EtP5 was prepared according to literature procedures.^[S1,S2] Activated crystalline EtP5 (EtP5 α) was recrystallized from tetrahydrofuran first and dried under vacuum at 75 °C for 12 h. ¹H NMR spectra were recorded on a Bruker AV500 instrument. Single crystal X-ray diffraction data were collected on a Bruker APEX II CCD detector using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The APEX3 software suite was used to manage data collection, reduction (SAINT), and absorption correction by the Multi-scan method (SADABS), structure determination via direct methods (SHLEX) and model refinement (SHELXL). All non-hydrogen atoms were refined anisotropically though many atoms required anisotropic displacement parameter restraints. All hydrogen atoms were refined with isotropic displacement coefficients and their positions ideally constrained. Thermogravimetric Analysis (TGA) was recorded using a TA Instrument TA-Q500 and the samples were heated under nitrogen gas at a rate of 10 °C /min. Powder X-ray diffraction (PXRD) data were measured with a powder X-ray diffractometer (D/max 2200vpc, Rigaku, Japan) using Cu K α radiation ($\lambda = 1.5046 \text{ \AA}$) with a range 5–40 °C. Gas chromatograms (GC) were tested by Agilent Technology INS-QC-07 in head-space injector.

2. Host-guest complexation in solution

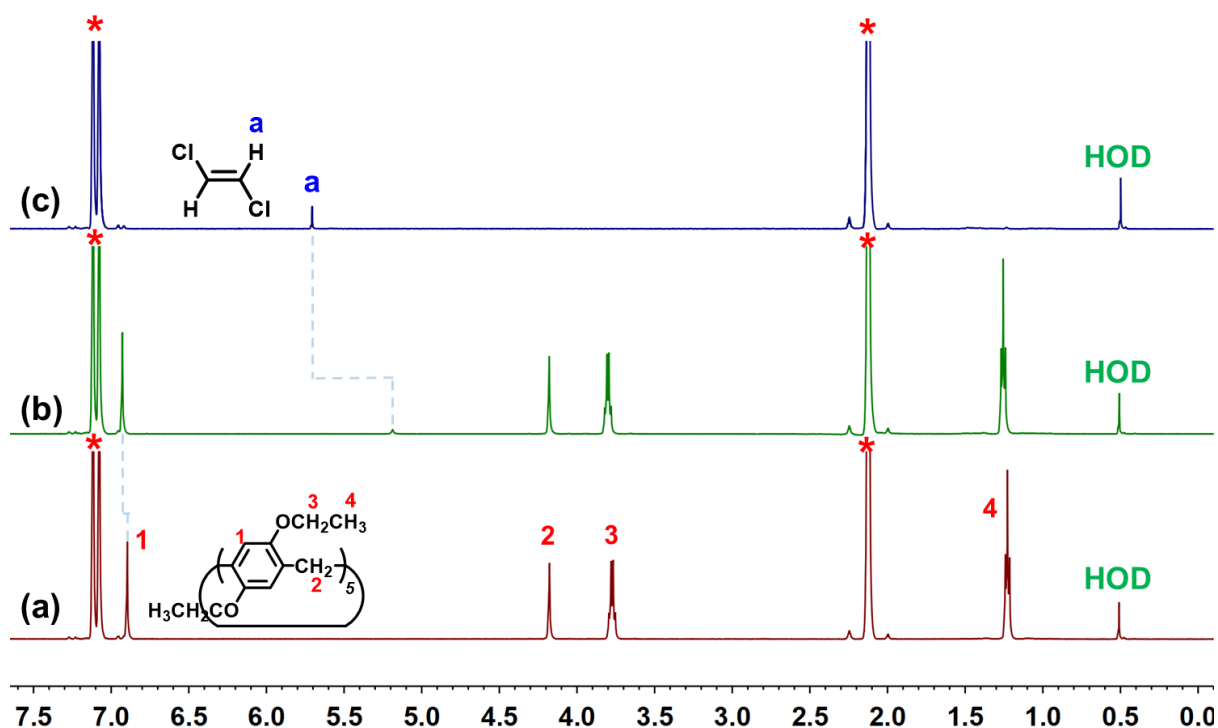


Figure S1. ¹H NMR spectra (500 MHz, 298 K) of (a) EtP5, (b) *trans*-DCE + EtP5, and (c) *trans*-DCE in *o*-xylene-*d*₁₀ at 5.0 mM. "*" indicates the solvent peaks.

Figure S1 shows ¹H NMR spectra of *trans*-DCE in the absence and presence of one eq. of EtP5 in *o*-xylene-*d*₁₀. Very large upfield shifts ($\Delta\delta = -0.52$ ppm for H_a) and broadening of peak was observed, indicative of a binding event. At the same time, EtP5 protons H₁ display downfield shifts ($\Delta\delta = 0.03$ ppm) due to de-shielding effects.

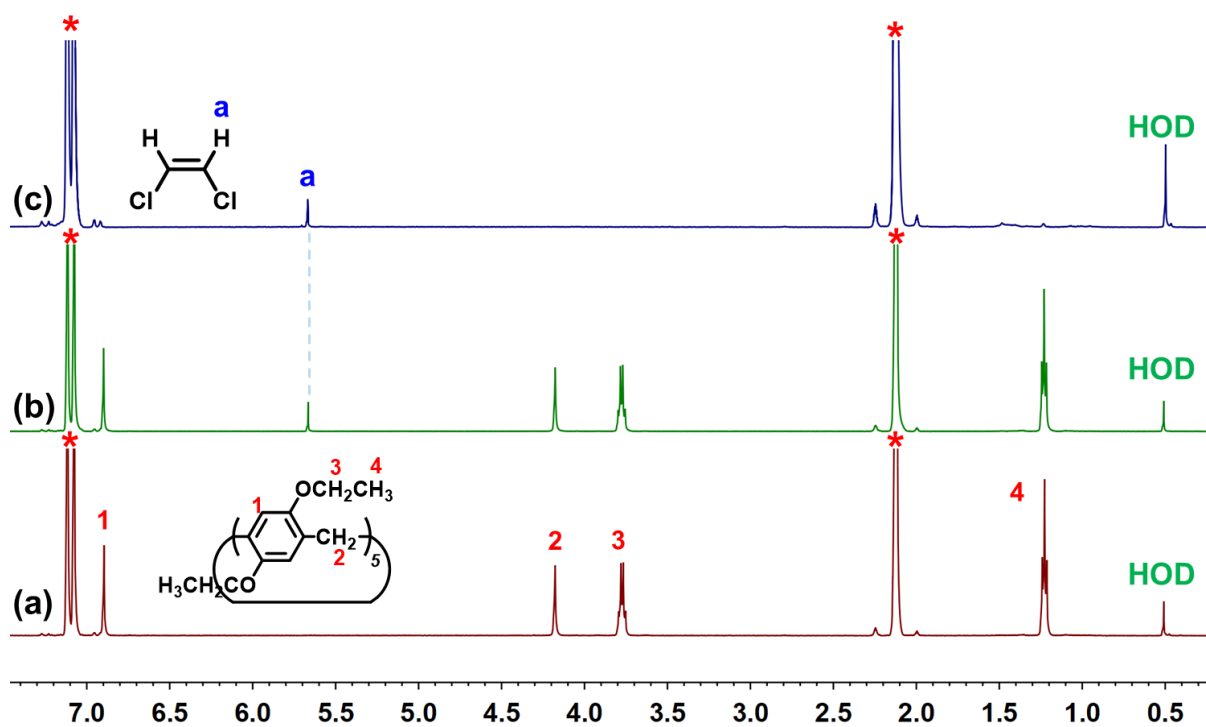


Figure S2. ^1H NMR spectra (500 MHz, 298 K) of (a) EtP5, (b) *cis*-DCE + EtP5, and (c) *cis*-DCE in o -xylene- d_{10} at 5.0 mM. “*” indicates the solvent peaks.

Figure S2 shows ^1H NMR spectra of *cis*-DCE in the absence and presence of one eq. of EtP5 in o -xylene- d_{10} . No signal changes were observed, indicating that no inclusion complex was formed.

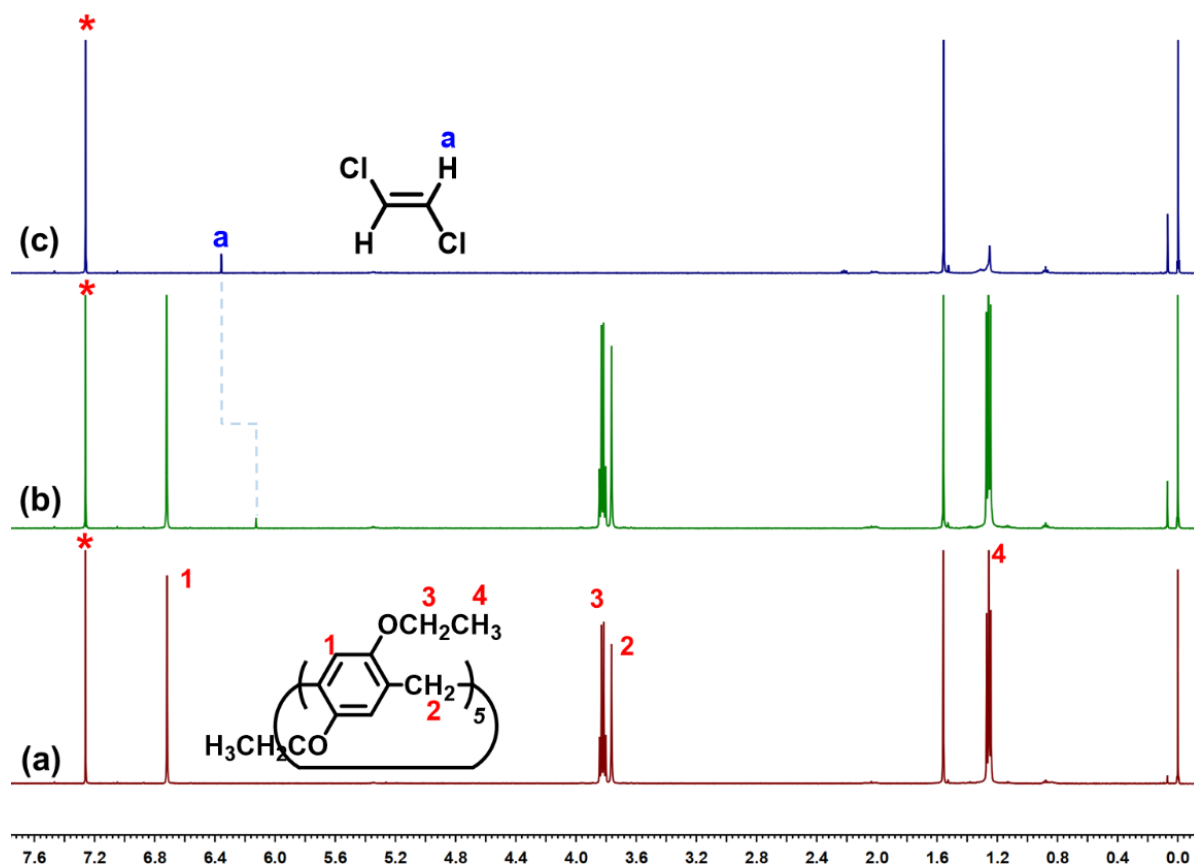


Figure S3. ¹H NMR spectra (500 MHz) of (a) EtP5, (b) EtP5 + *trans*-DCE, (c) *trans*-DCE at 5.0 mM in CDCl₃. “*” indicates the solvent peaks.

Figure S3 shows ¹H NMR spectra of *trans*-DCE in the absence and presence of one eq. of EtP5 in CDCl₃. The upfield shifts ($\Delta\delta = -0.25$ ppm for H_a) was observed, indicative of a binding event.

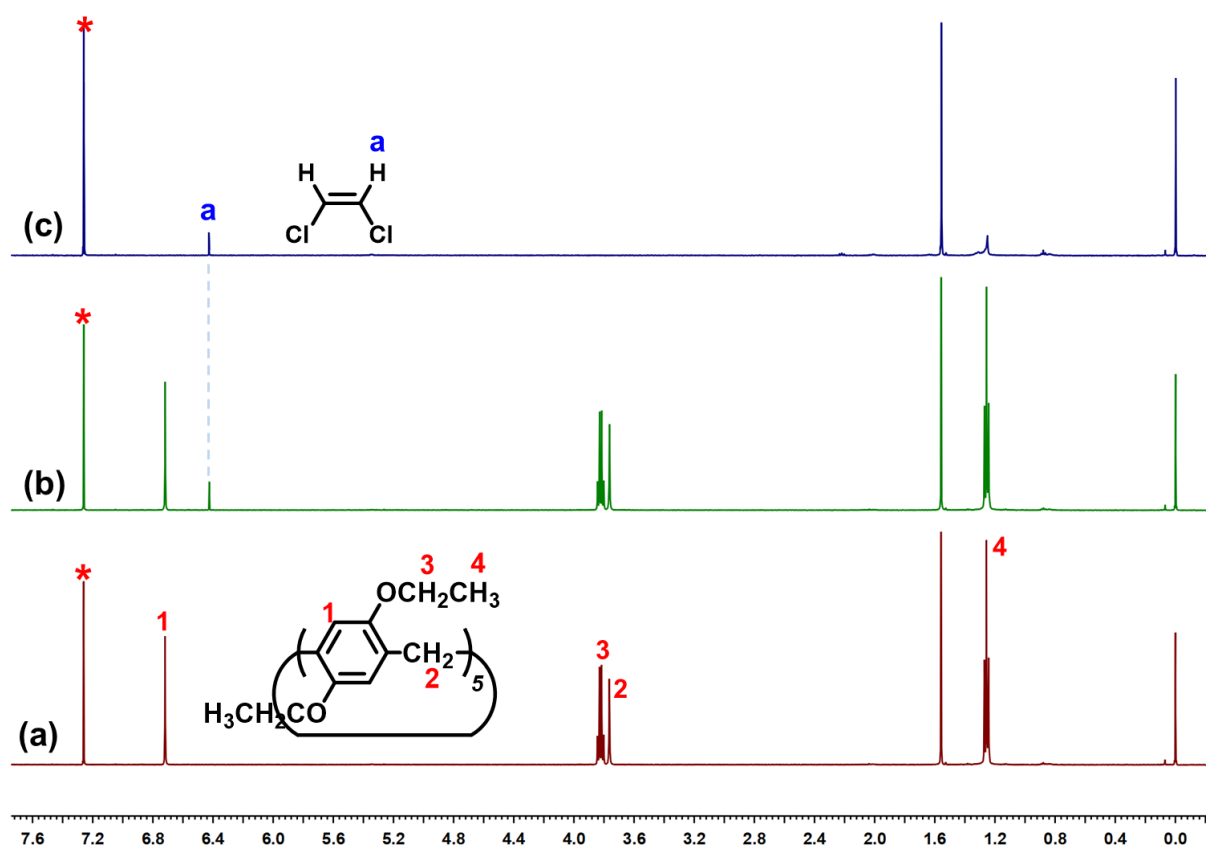


Figure S4. ^1H NMR spectra (500 MHz) of (a) EtP5, (b) EtP5 + *cis*-DCE, (c) *cis*-DCE at 5.0 mM in CDCl_3 . "*" indicates the solvent peaks.

Figure S4 shows ^1H NMR spectra of *cis*-DCE in the absence and presence of one eq. of EtP5 in CDCl_3 . No signal changes were observed, indicating that no inclusion complex was formed.

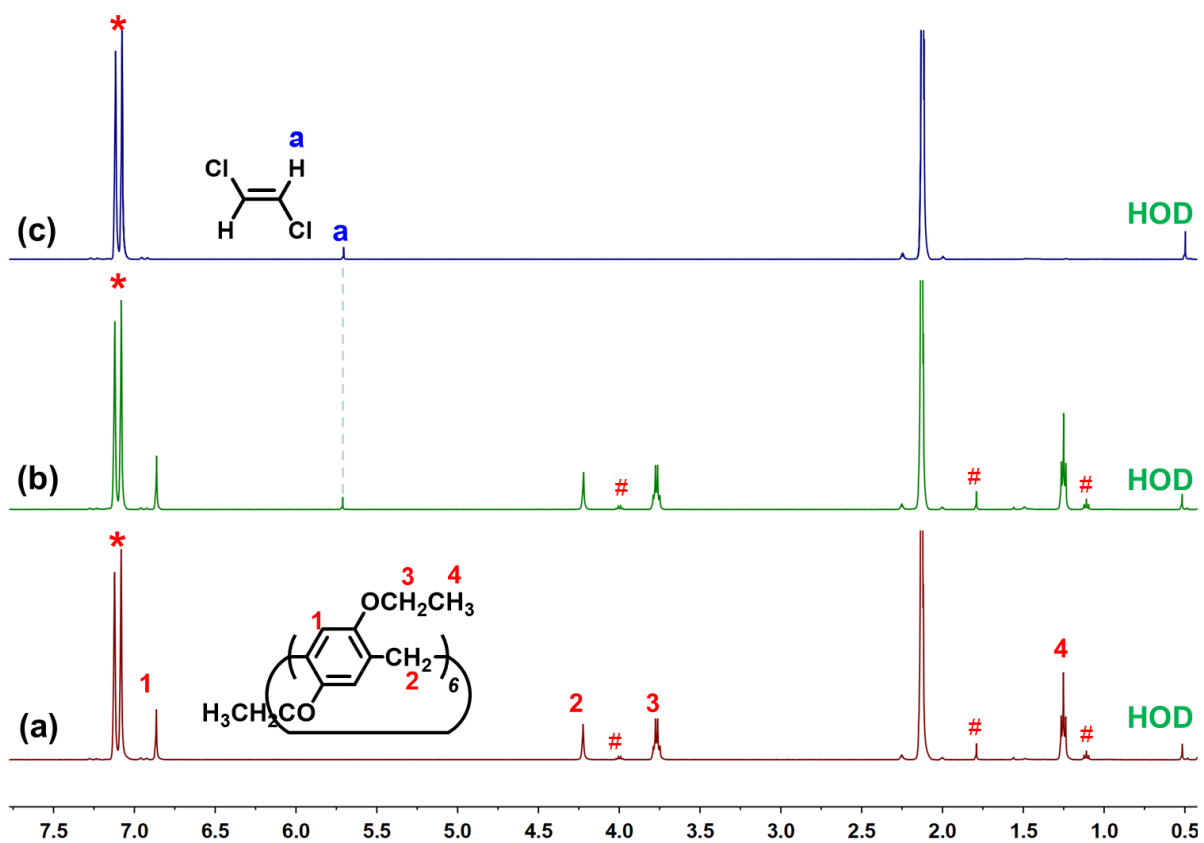


Figure S5. ^1H NMR spectra (500 MHz, 298 K) of (a) EtP6, (b) *trans*-DCE + EtP6, and (c) *trans*-DCE in o -xylene- d_{10} at 5.0 mM. "*" indicates the solvent peaks. "#" indicates the solvent peaks of ethyl acetate.

Figure S5 shows ^1H NMR spectra of *trans*-DCE in the absence and presence of one eq. of EtP6 in o -xylene- d_{10} . No signal changes were observed, indicating that no inclusion complex was formed.

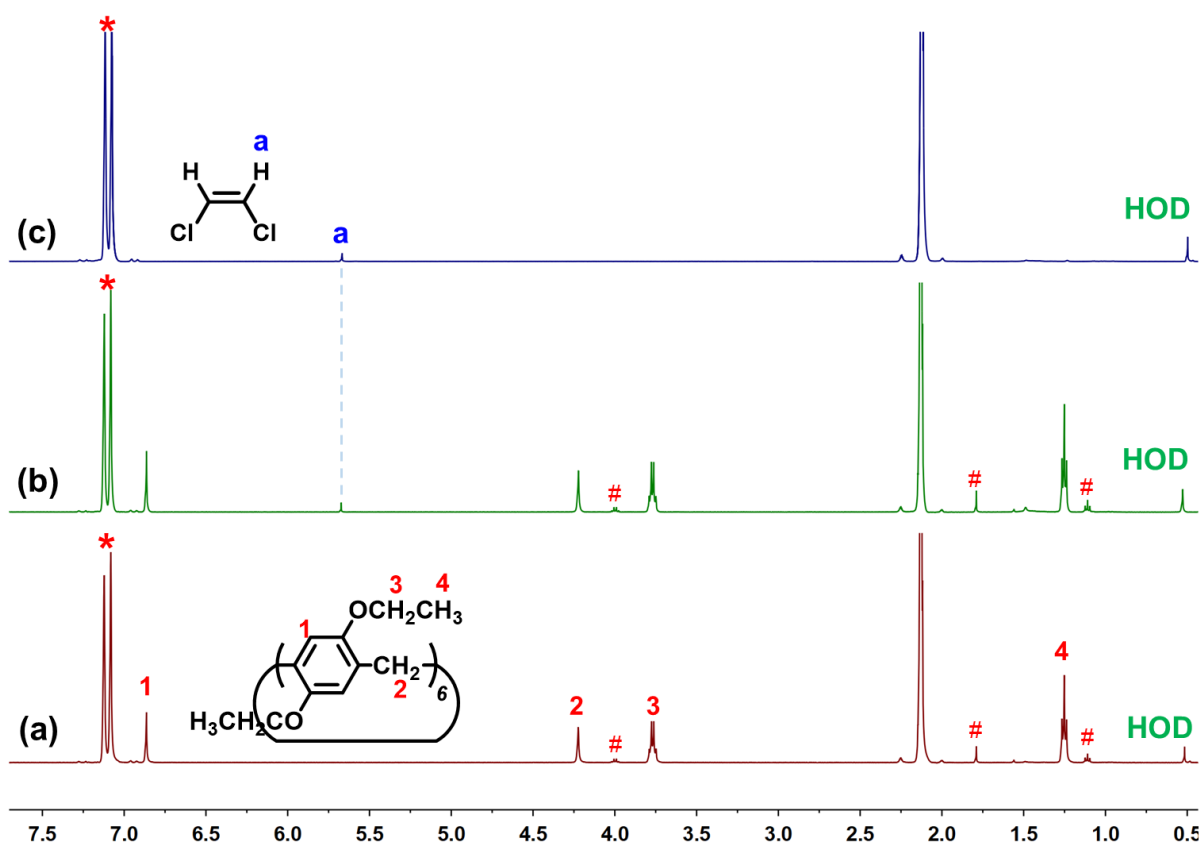


Figure S6. ^1H NMR spectra (500 MHz, 298 K) of (a) EtP6, (b) *cis*-DCE + EtP6, and (c) *cis*-DCE in o -xylene- d_{10} at 5.0 mM. "*" indicates the solvent peaks. "#" indicates the solvent peaks of ethyl acetate.

Figure S6 shows ^1H NMR spectra of *cis*-DCE in the absence and presence of one eq. of EtP6 in o -xylene- d_{10} . No signal changes were observed, indicating that no inclusion complex was formed.

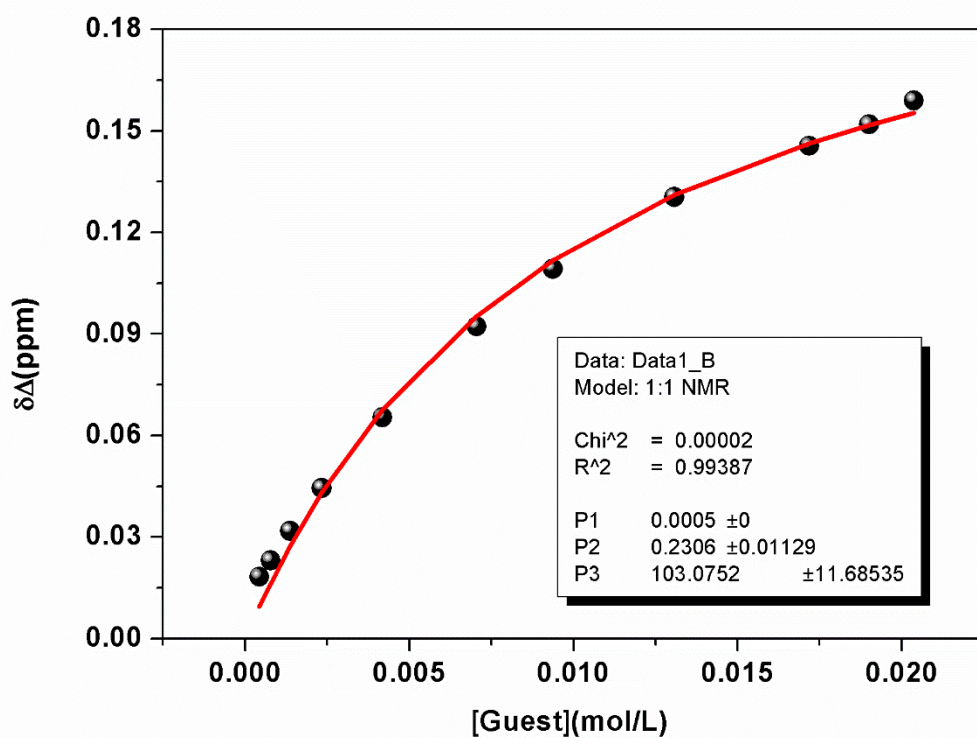


Figure S7. The non-linear curve-fitting (NMR titrations, 500 MHz) for the complexation of EtP5 host (0.50 mM) with *trans*-DCE in *o*-xylene-*d*₁₀ at 298 K. The concentration of *trans*-DCE was 0.19, 0.58, 1.33, 2.76, 5.38, 9.82, 13.4, 19.0, 26.1, 30.5, 33.8 mM.

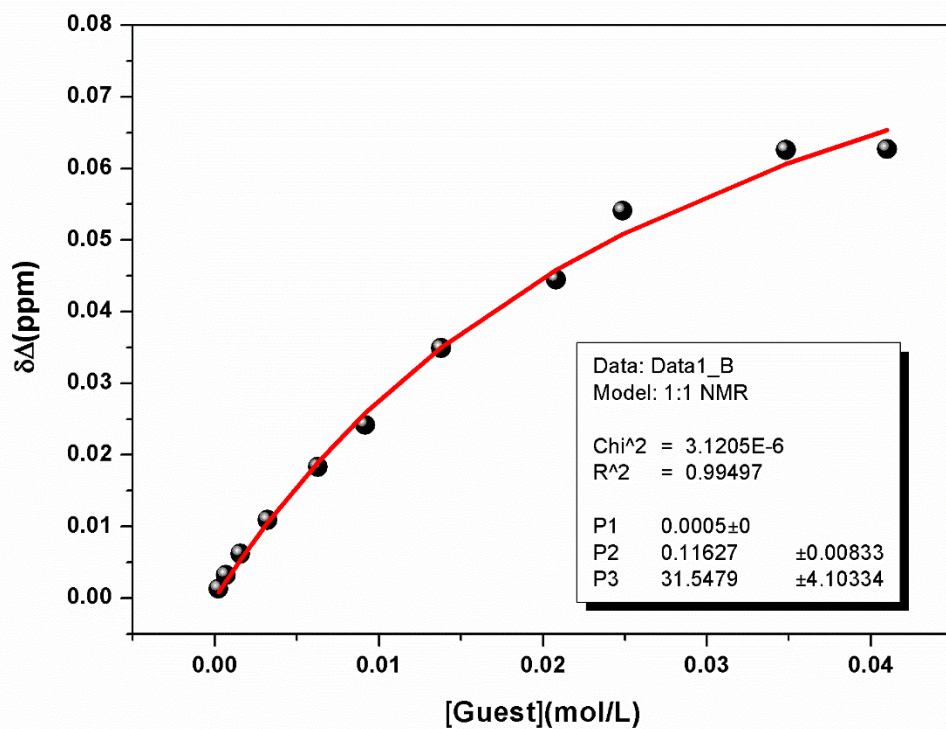


Figure S8. The non-linear curve-fitting (NMR titrations, 500 MHz) for the complexation of EtP5 host (0.50 mM) with *trans*-DCE in CDCl₃ at 298 K. The concentration of *trans*-DCE was 0.23, 0.67, 1.55, 3.22, 6.28, 9.17, 13.8, 20.8, 24.9, 34.8, 41.0 mM.

3. Crystal data and structures

Table S1. Crystal data and structure refinement for *trans*-DCE@EtP5.

Identification code	<i>trans</i> -DCE@EtP5	
Empirical formula	C ₁₁₈ H ₁₄₇ Cl ₈ O ₂₀	
Formula weight	2168.95	
Temperature	153.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 22.214(4) Å	$\alpha = 90^\circ$
	<i>b</i> = 20.800(4) Å	$\beta = 100.33(3)^\circ$
	<i>c</i> = 25.875(5) Å	$\gamma = 90^\circ$
Volume	11762(4) Å ³	
Z	4	
Density (calculated)	1.225 Mg/m ³	
Absorption coefficient	0.256 mm ⁻¹	
F(000)	4604	
Crystal size	0.34 x 0.23 x 0.21 mm ³	
Theta range for data collection	0.932 to 25.000°.	
Index ranges	-23 ≤ <i>h</i> ≤ 26, -24 ≤ <i>k</i> ≤ 22, -30 ≤ <i>l</i> ≤ 30	
Reflections collected	62961	
Independent reflections	20645 [R(int) = 0.0735]	
Completeness to theta = 25.000°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7650	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	20645 / 330 / 1437	
Goodness-of-fit on F ²	1.139	
Final R indices [I > 2σ(I)]	R1 = 0.1578, wR2 = 0.4057	
R indices (all data)	R1 = 0.1781, wR2 = 0.4279	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.729 and -0.821 e.Å ⁻³	
CCDC	2025010	

Table S2. Crystal data and structure refinement for guest free EtP5.

Identification code	mo_dd18146_0m	
Empirical formula	C ₅₅ H ₇₀ O ₁₀	
Formula weight	891.11	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7560(9) Å	α = 97.980(2)°
	b = 14.7694(11) Å	β = 111.813(2)°
	c = 15.2714(12) Å	γ = 107.160(2)°
Volume	2450.0(3) Å ³	
Z	2	
Density (calculated)	1.208 Mg/m ³	
Absorption coefficient	0.082 mm ⁻¹	
F(000)	960	
Crystal size	0.200 x 0.170 x 0.130 mm ³	
Theta range for data collection	2.400 to 26.000°.	
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18	
Reflections collected	40313	
Independent reflections	9620 [R(int) = 0.0608]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6249	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9620 / 0 / 597	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2σ(I)]	R1 = 0.0527, wR2 = 0.1112	
R indices (all data)	R1 = 0.0916, wR2 = 0.1326	
Extinction coefficient	0.0081(8)	
Largest diff. peak and hole	0.347 and -0.227 e.Å ⁻³	
CCDC	1905571	

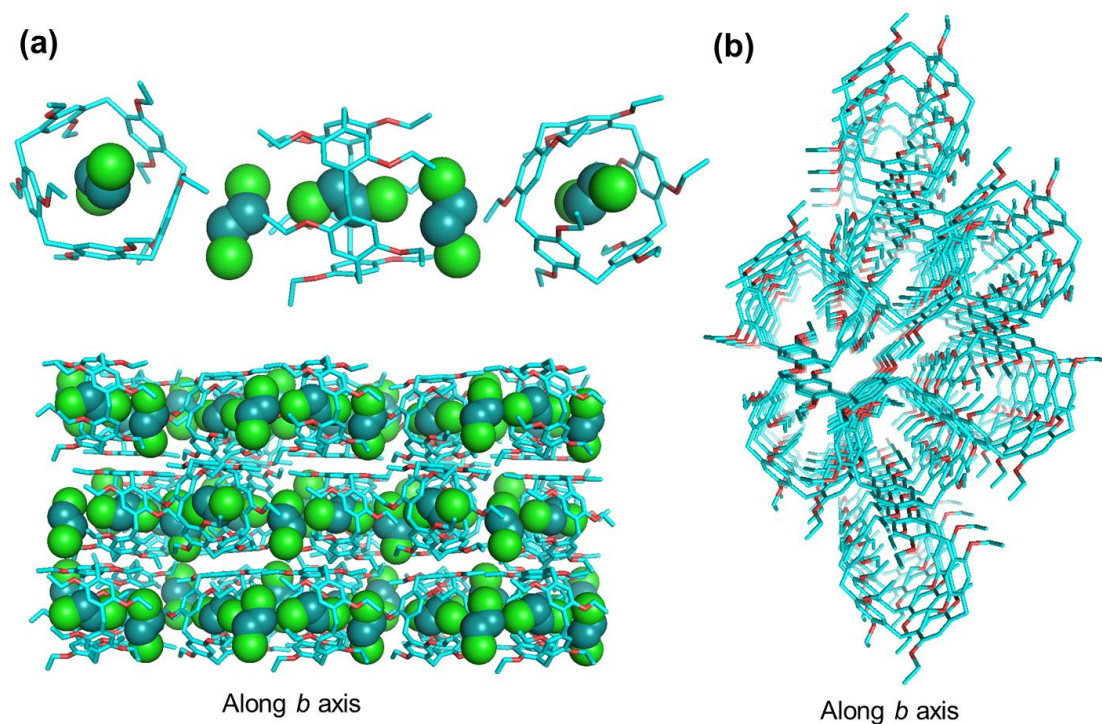


Figure S9. Stacking modes of (a) *trans*-DCE@EtP5 and (b) guest-free EtP5 crystal structure obtained from a *cis*-DCE solution.

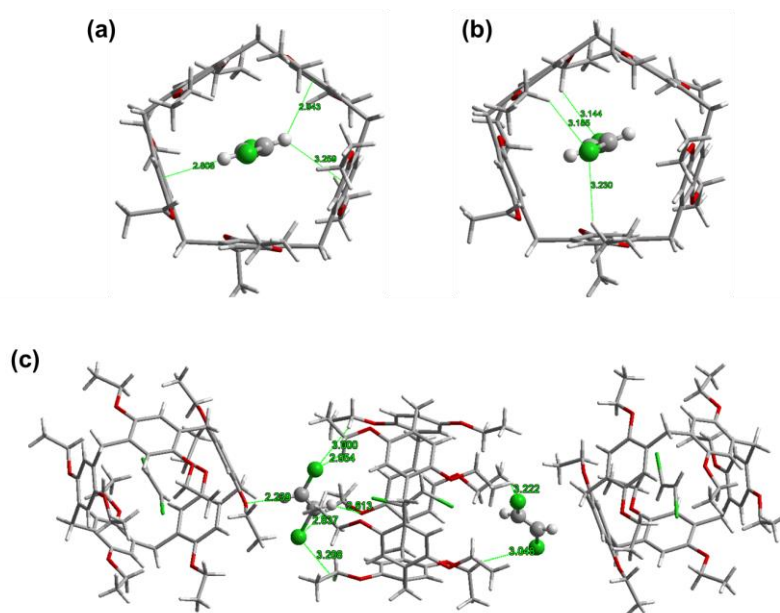


Figure S10. Noncovalent bonding parameters of *trans*-DCE@EtP5: Hydrogen bond distances (\AA) of C–H... π (a) and C–H...Cl (b) between *trans*-DCE located in EtP5' cavity and EtP5, and C–H...O/Cl between *trans*-DCE located outside EtP5' cavity and EtP5 (c).

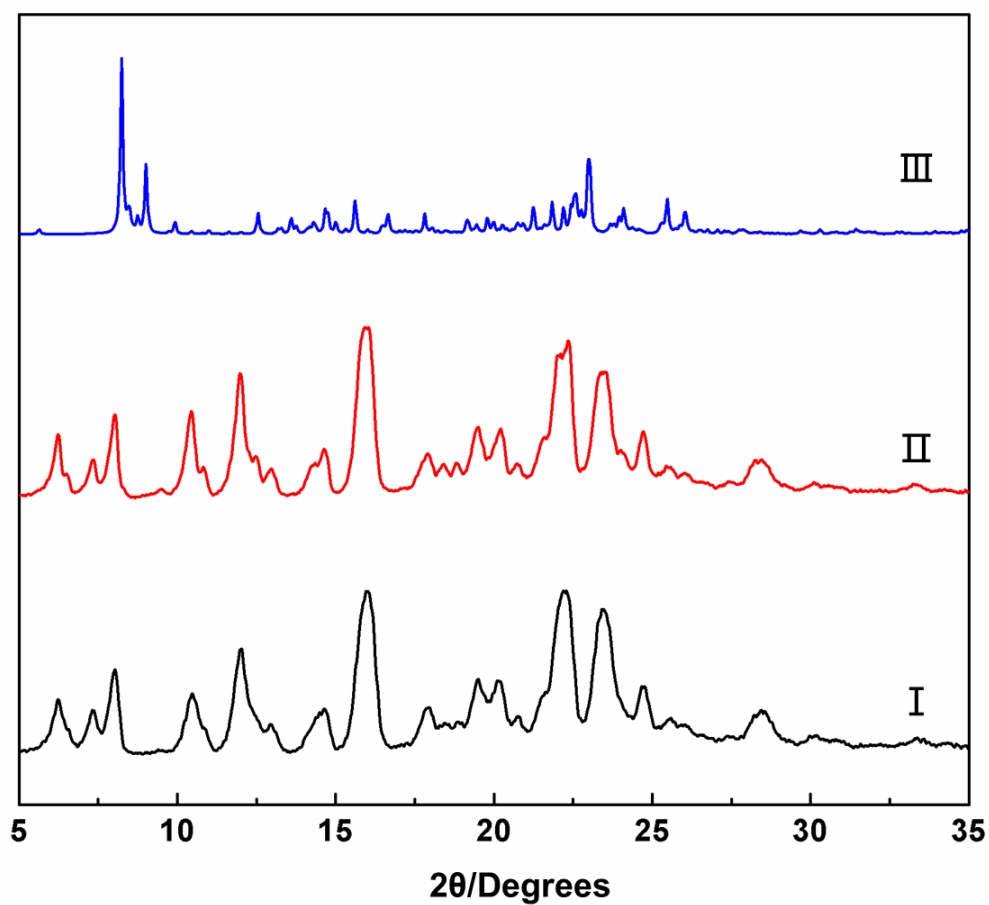


Figure S11. PXRD patterns of EtP5: (I) EtP5 crystals crystallized in *cis*-DCE solution; (II) EtP5 α ; (III) simulated from single-crystal structure of THF@EtP5^{S3}.

4. Vapor adsorption experiments

For single-component *cis*-/*trans*-DCE or *cis*- and *trans*- DCE isomer mixtures (50:50 *v/v cis:trans*-DCE) adsorption experiment, an open 3 mL vial containing 5.0 mg of EtP5 α adsorbent was placed in a sealed 20 mL vial containing 1 mL of *cis*-DCE or *trans*-DCE isomer. Uptake amount in the EtP5 α crystals was monitored over time by ^1H NMR spectra by completely dissolving the crystals in CDCl_3 . Desorption experiments after uptake saturation were carried out by TGA analysis. The purity of *trans*-DCE was measured by GC. Before measurements, the crystals were heated at 30 °C to remove the surface-physically adsorbed vapor molecules.

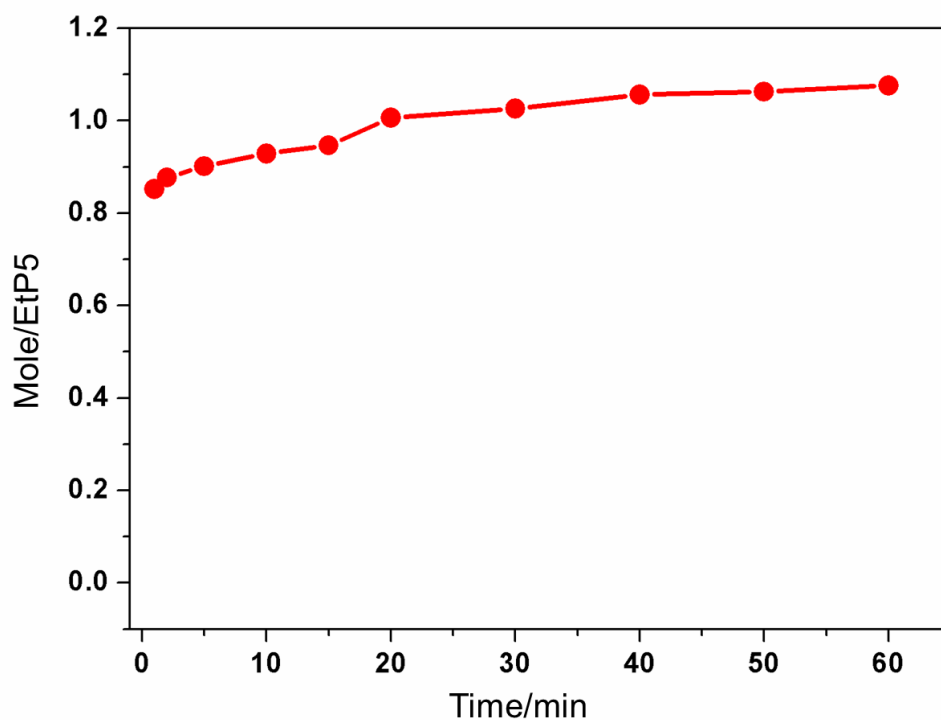


Figure S12. Time-dependent solid–vapor sorption plots of EtP5 α for single-component *trans*-DCE vapor.

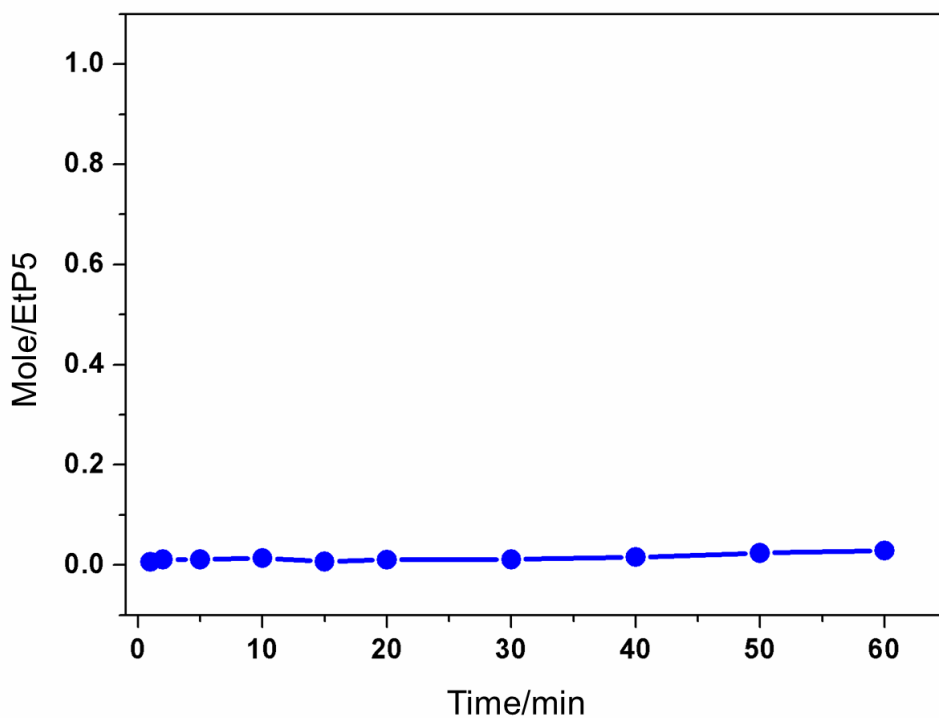


Figure S13. Time-dependent solid-vapor sorption plots of EtP5 α for single-component *cis*-DCE vapor.

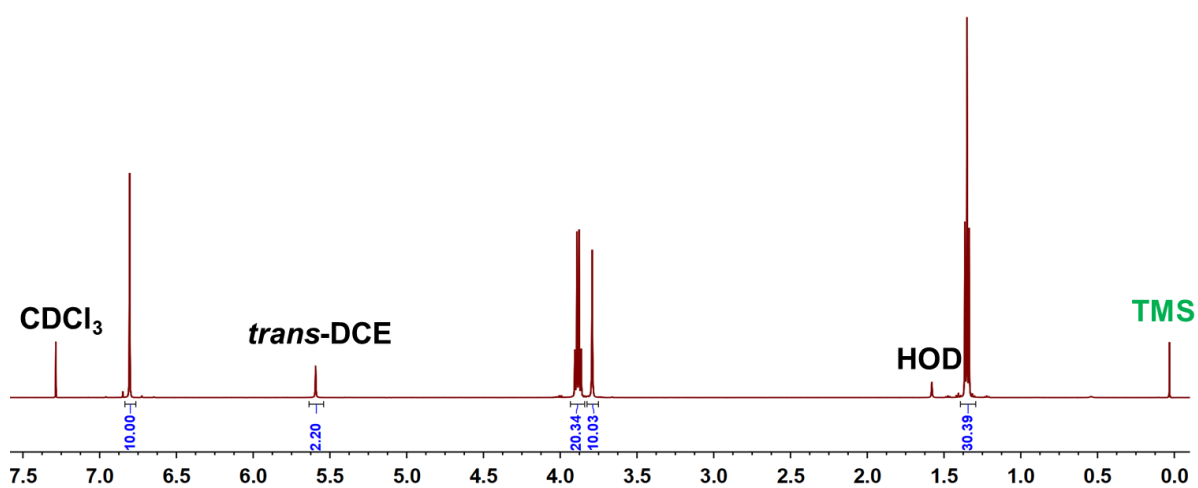


Figure S14. ¹H NMR spectrum (500MHz, 298K, CDCl₃) of EtP5 α after adsorption of *trans*-DCE for 60 minutes.

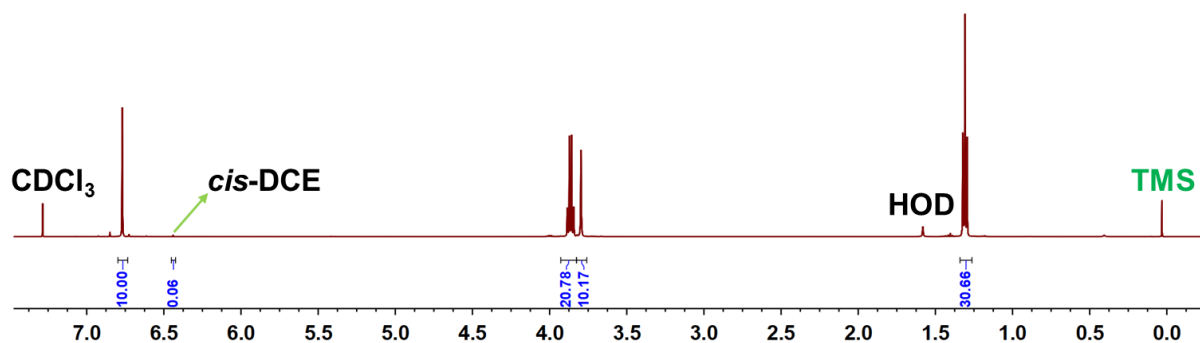


Figure S15. ^1H NMR spectrum (500MHz, 298K, CDCl_3) of $\text{EtP5}\alpha$ after adsorption of *cis*-DCE for 60 minutes.

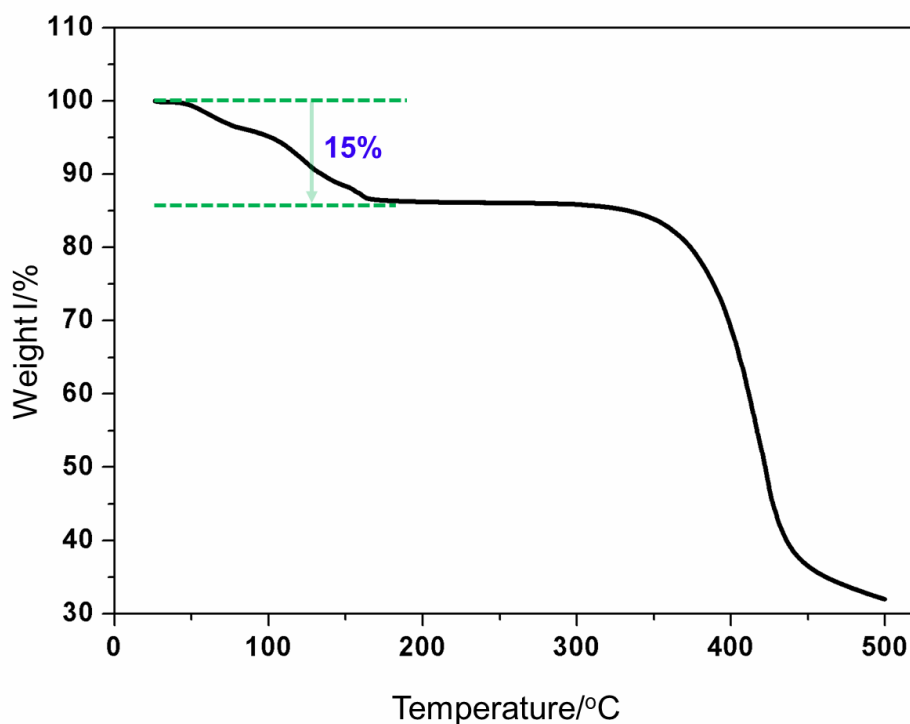


Figure S16. Thermogravimetric analysis of $\text{EtP5}\alpha$ after adsorption of *trans*-DCE. The weight loss was calculated as 1.1 *trans*-DCE molecules per $\text{EtP5}\alpha$ molecule.

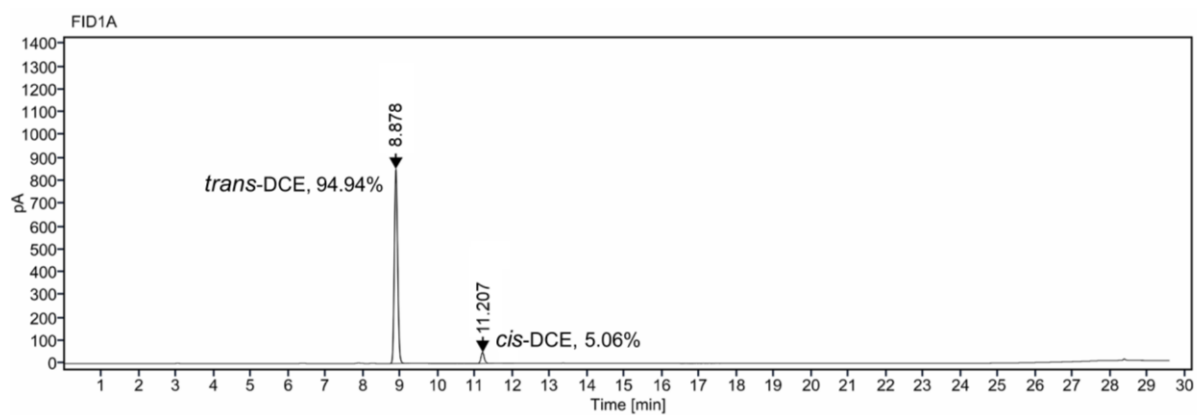


Figure S17. Relative *cis*- and *trans*-DCE uptake in EtP5 α after 60 minutes using GC.

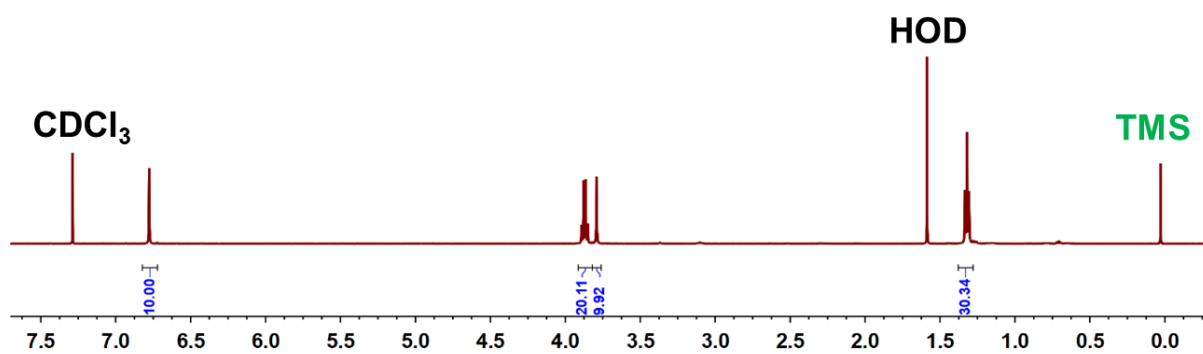


Figure S18. ¹H NMR spectrum (500MHz, 298K, CDCl₃) of EtP5 α after desorption of *trans*-DCE by heating at 75 °C under vacuum for 12 h.

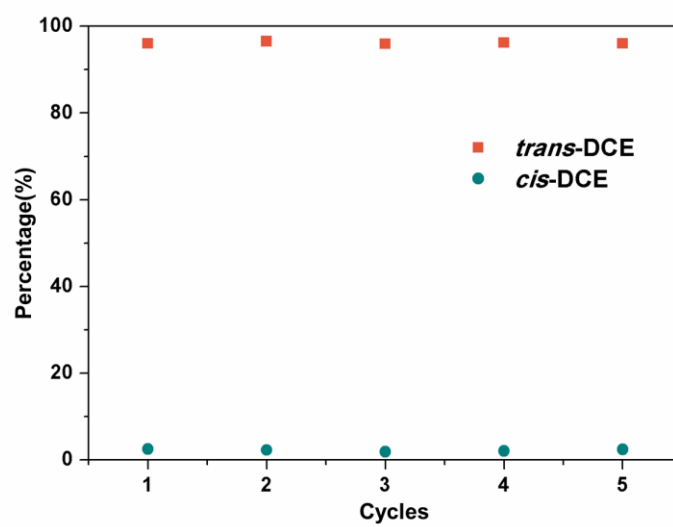


Figure S19. Relative uptake ratios of EtP5 α towards *cis/trans*-DCE (50:50 v/v) mixtures after five recycles.

5. Self-sorting separation experiments

For self-sorting adsorption experiment for *cis*- and *trans*- DCE isomer mixtures (50:50 *v/v cis:trans*-DCE), two open 3 mL vials containing 5.0 mg of EtP5 α and 5.0 mg MeBP3 α adsorbent were placed in a sealed 50 mL vessel containing 5 mL of *cis*-DCE and *trans*-DCE isomers mixture. Uptake amounts in the EtP5 α and MeBP3 α crystals were monitored over time by ^1H NMR spectra by completely dissolving the crystals in CDCl_3 . The purity of *cis*- or *trans*-DCE was measured by GC. Before measurements, the crystals were heated at 30 $^\circ\text{C}$ to remove the surface-physically adsorbed vapor molecules.

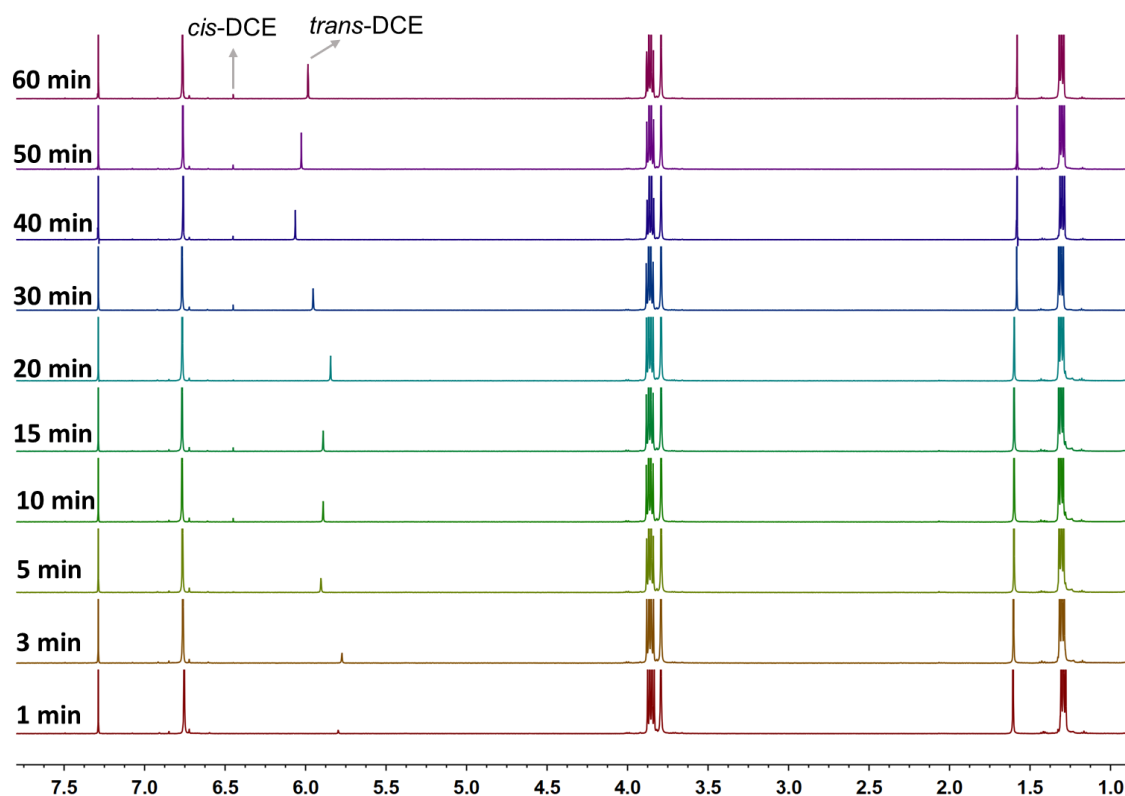


Figure S20. Time-dependent ^1H NMR self-sorting spectra (500 MHz, CDCl_3) of EtP5 α after uptake of *cis/trans*-DCE (50:50 *v/v*) mixtures vapor. The relative uptake of *cis* and *trans*-DCE by EtP5 α is plotted in Figure 4.

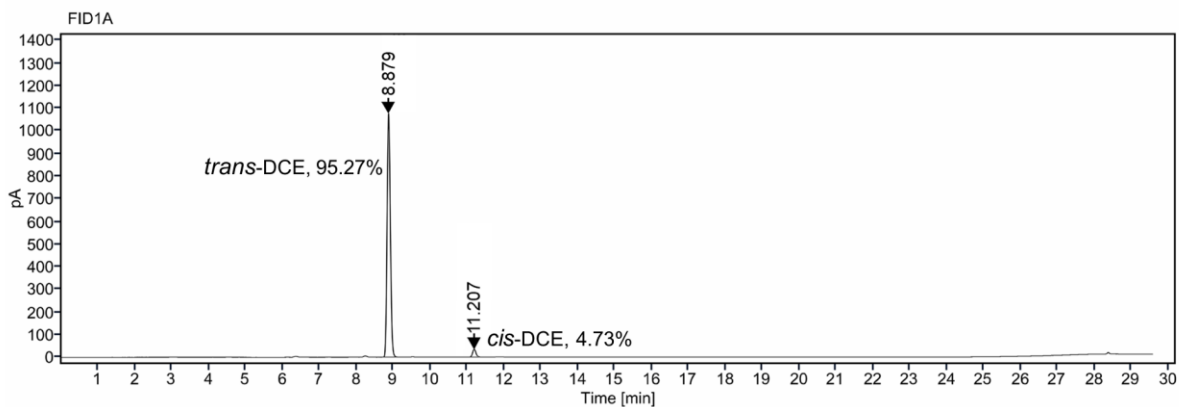


Figure S21. Relative *cis*- and *trans*-DCE uptake in EtP5 α after 60 minutes using GC.

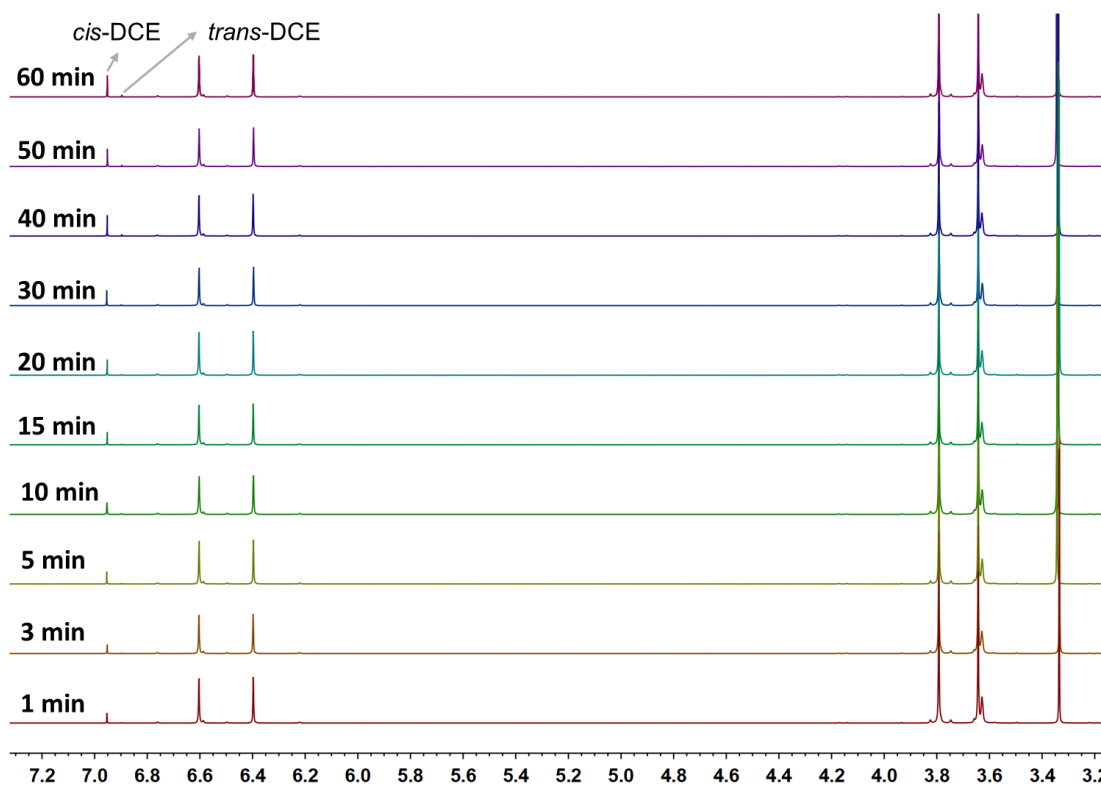


Figure S22. Time-dependent ^1H NMR self-sorting spectra (500 MHz, d_6 -DMSO) of MeBP3 α after uptake of *cis/trans*-DCE (50:50 v/v) mixtures vapor. The relative uptake of *cis* and *trans*-DCE by MeBP3 α is plotted in Figure 4.

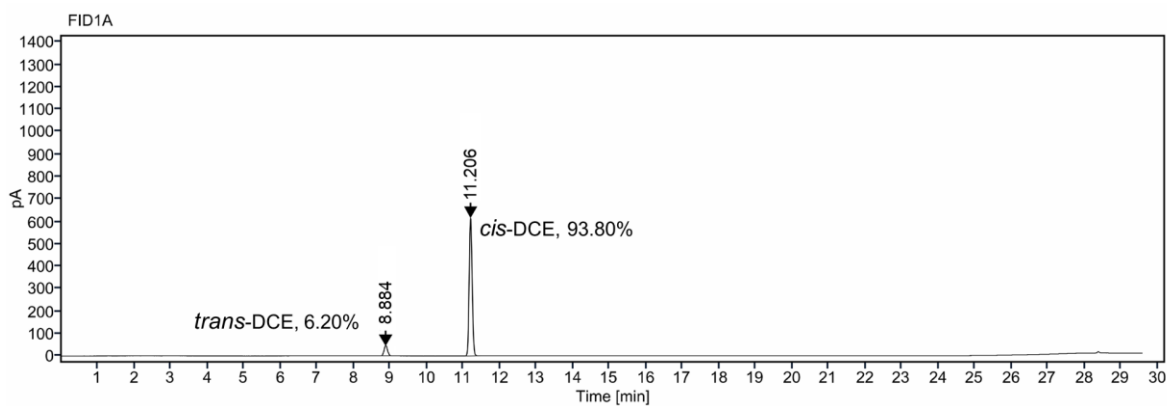


Figure S23. Relative *cis*- and *trans*-DCE uptake in MeBP3 α after 60 minutes using gas chromatography.

6. References

- (S1) T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto. *J. Am. Chem. Soc.*, 2008, **130**, 5022–5023.
- (S2) X.-B. Hu, Z. Chen, L. Chen, L. Zhang, J.-L. Hou and Z.-T. Li, *Chem. Commun.*, 2012, **48**, 10999–11001.
- (S3) K. Jie, M. Liu, Y. Zhou, M. A. Little, S. Bonakala, S. Y. Chong, A. Stephenson, L. Chen, F. Huang, and A. I. Cooper. *J. Am. Chem. Soc.* **2017**, *139*, 2908–2911.