Electronic Supplementary Information

Adsorptive Separation of Cyclohexanol and Cyclohexanone by Nonporous Adaptive Crystals of RhombicArene

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I. General Information

$^1$H and $^{13}$C NMR spectra were recorded with a Bruker Avance 400 spectrometer at 25 °C and were internally referenced to residual protio solvent signals (for example, CDCl$_3$ was referenced at 7.26 and 77.16 ppm, respectively, see: G. R. Fulmer, et al Organometallics 2010, 29, 2176). Data for $^1$H NMR were reported as follows: chemical shift (δ ppm), integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constant (Hz) when applicable. All $^{13}$C NMR spectra were recorded with complete proton decoupling. High-resolution mass spectrometry experiments were performed with an AB Sciex MALDI-TOF/TOF 5800 mass spectrometer using TCNQ matrix (for MALDI). GC analysis was carried out on a Shimadzu-2010 plus instrument equipped with an FID detector and a SH-RTX-5 columns (crossbond 5% diphenyl/95% dimethyl polysiloxane; length: 30 m; diameter: 0.25 mm; film thickness: 0.25 μm). Chiral stationary phase HPLC was performed on a Shimadzu 20A instrument equipped with a multiple-wavelength UV/Vis diode array detector. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Focus X-ray diffractometer equipped with a Cu Kα radiation (λ = 1.5405 Å) source. Thermogravimetric analysis (TGA) was carried out on an SDT Q600 V20.9 Build 20 using DSC-TGA module.

All reactions were carried out using flame-dried glassware under a nitrogen atmosphere unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 200-300 mesh silica gel. HPLC-grade tetrahydrofuran, dichloromethane, diethyl ether, toluene, and hexanes were purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology, Inc.). Deionized water was degassed by bubbling with nitrogen balloon for 20 min prior to use as reaction solvent. Chemical reagents were purchased from Adamas, Acros, Bidepharm, Energy Chemicals, InnoChem, TCI, and Strem, and were used as received.
II. Synthesis and Characterization

Compound (S)-S1

To a 100 mL round-bottom flask equipped with a stir bar was sequentially added (S)-H₈-BINOL (1.00 g, 3.40 mmol, 1.00 equiv), CH₂Cl₂ (60 mL), morpholine (1.7 mL, 20 mmol, 5.8 equiv), and I₂ (1.7 g, 6.8 mmol, 2.0 equiv) at 25 °C under nitrogen. The reaction mixture was stirred at 25 °C for 5 h, before quenched with HCl (2 N, 10 mL). The aqueous phase was extracted with CH₂Cl₂. The combined organic layers were sequentially washed with saturated sodium thiosulfate solution and brine, and dried over Na₂SO₄. The solvent was then removed under reduced pressure. Purification using silica gel column chromatography (eluent: petroleum ether: ethyl acetate = 15/1) afforded compound (S)-S1 (1.75 g, 94%) as a white solid. Characterization data were identical to the literature (Angew. Chem. Int. Ed. 2016, 55, 331).

¹H NMR (400 MHz, CDCl₃) δ 7.51 (s, 2H), 4.96 (s, 2H), 2.72 (t, J = 5.8 Hz, 4H), 2.32-2.21 (m, 2H), 2.14-2.02 (m, 2H), 1.76-1.60 (m, 8H).

Compound (S)-2

In a nitrogen-filled glove box, Pd(PPh₃)₄ (53 mg, 0.046 mmol, 5 mol%), (S)-S1 (500 mg, 0.92 mmol, 1.0 equiv), boronic acid S2 (832 mg, 4.6 mmol, 5.0 equiv), and Na₂CO₃ (505 mg, 4.8 mmol, 5.2 equiv) were sequentially added to a 40 mL glass vial equipped with a stir bar. Anhydrous 1,2-dimethoxyethane (8.0 mL) was then added to the reaction mixture. The reaction vial was sealed with a teflon-lined cap, and transferred out of the glove box. Degassed water (0.5 mL) was added to the reaction vial by a syringe. The reaction mixture was stirred at 90 °C for 16 h, cooled down to room temperature, and filtered through a short pad of Celite with the aid of ethyl
acetate (100 mL). The combined organic layers were washed with brine, and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure. Purification using silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 5/1) afforded compound (S)-2 (412.0 mg, 79%) as a white solid. Characterization data were identical to the literature (Org. Lett. 2009, 11, 2441).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (s, 2H), 6.99 (d, $J = 3.0$ Hz, 2H), 6.92 (d, $J = 8.9$ Hz, 2H), 6.87 (dd, $J = 8.9$, 3.0 Hz, 2H), 5.92 (br, s, 2H), 3.81 (s, 6H), 3.77 (s, 6H), 2.81 - 2.74 (m, 4H), 2.55 - 2.39 (m, 8H), 1.87 - 1.67 (m, 16H).

RhombicArene (1)

To a 500 mL round-bottom flask equipped with a stir bar was sequentially added (S)-2 (120 mg, 0.21 mmol, 1.0 equiv), CH$_2$Cl$_2$ (240 mL), paraformaldehyde (38 mg, 1.3 mmol, 6.0 equiv), and 1,4-cyclohexanedione (11.9 mg, 0.11 mmol, 0.5 equiv) under nitrogen. Boron trifluoride diethyl etherate (52 μL, 0.42 mmol, 2.0 equiv) was then added to the reaction mixture at 25 °C. The mixture was stirred at 25 °C for 5 h before quenched by water (6 mL). The organic phase was washed with saturated aqueous NaHCO$_3$ and brine, dried over anhydrous Na$_2$SO$_4$, and concentrated. Purification using silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 3/1) afforded compound (S,S)-1 (25.4 mg, 21%) as a white solid. The (R,R)-1 was prepared from (R)-2 under the same condition.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (s, 4H), 7.01 (s, 4H), 6.63 (s, 4H), 5.53 (br, s, 4H), 3.90 (s, 4H), 3.73 (s, 12H), 3.63 (s, 12H), 2.89-2.74 (m, 8H), 2.54-2.39 (m, 8H), 1.87-1.67 (m, 16H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.1, 149.0, 148.5, 136.1, 129.7, 129.6, 129.3, 125.3, 124.1, 123.7, 115.1, 114.7, 56.6, 55.8, 31.7, 29.4, 27.5, 23.21, 23.18;

IR (Film): 3436, 2933, 2822, 1638, 1485, 1404, 1173, 1083 cm$^{-1}$;

HRMS (MALDI): [M+Na]$^+$ calcld for C$_{74}$H$_{76}$NaO$_{12}$ 1179.5229, found 1179.5187;

$[\alpha]_D^{20} = -64.4^\circ$ (c = 0.1, CHCl$_3$, prepared from (S)-2).
Table S1. Optimizations for the synthesis of 1.

| entry | BF$_3$·OEt$_2$ (equiv) | 1,4-cyclohexanedione (equiv) | NMR yield (%)$^{[a]}$ |
|-------|----------------------|-------------------------------|---------------------|
| 1     | 1.0                  | 0                            | 12                  |
| 2     | 2.0                  | 0                            | 11                  |
| 3     | 3.0                  | 0                            | 9                   |
| 4     | 1.0                  | 0.5                          | 16                  |
| 5     | 2.0                  | 0.5                          | 24                  |
| 6     | 3.0                  | 0.5                          | 10                  |

$^{[a]}$ The yields were determined by $^1$H NMR using an internal standard ($N,N$-dimethyl trifluoroacetamide).

Table S2. Screening of the amount of 1,4-cyclohexanedione for the synthesis of 1.

| entry | BF$_3$·OEt$_2$ (equiv) | 1,4-cyclohexanedione (equiv) | NMR yield (%)$^{[a]}$ |
|-------|----------------------|-------------------------------|---------------------|
| 1     | 2.0                  | 0                            | 11                  |
| 2     | 2.0                  | 0.25                         | 14                  |
| 3     | 2.0                  | 0.5                          | 24                  |
| 4     | 2.0                  | 1.0                          | 21                  |
| 5     | 2.0                  | 2.0                          | 10                  |

$^{[a]}$ The yields were determined by $^1$H NMR using an internal standard ($N,N$-dimethyl trifluoroacetamide).
Table S3. Evaluations of starting materials for the synthesis of 1.

| Entry | Starting Material | NMR yield of 1 (%)<sup>[[a]]</sup> |
|-------|-------------------|-----------------------------------|
| 1     | (S)-2             | 24%                               |
| 2     | (R)-2             | 20%                               |
| 3     | rac-2             | complex mixture compound 1 was not identified |

<sup>[[a]]</sup> The yields were determined by <sup>1</sup>H NMR using an internal standard (N,N-dimethyl trifluoroacetamide).

Figure S1. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 298 K) of 1.
Figure S2. $^{13}$C NMR spectrum (CDCl$_3$, 101 MHz, 298 K) of 1.
III. X-ray Crystallography and Computational Analysis

The X-ray crystallographic analysis was obtained on a Bruker D8 VENTURE diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å). Data were corrected for absorption effects using the Multi-Scan method (SADABS). Data collection and reduction were performed using the APEX 3 software. The structure was solved and refined using the Bruker SHELXTL Software Package. The crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques using all unique data. The SQUEEZE algorithm was used for any solvent molecules that could not be restrained properly. Crystallographic data were deposited at the Cambridge Crystallographic Data Center (CCDC). The data can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

3.1 RhombicArene (1)

Single crystals of 1 suitable for X-ray crystallography were obtained by slow evaporation of a solution of 1 in mixed chloroform/MeCN (1:3) at 25 °C. Crystallographic data were deposited at the Cambridge Crystallographic Data Center (CCDC 2067429).

Table S4. Crystal data and structure refinement for 1.

| Property                        | Value                                    |
|---------------------------------|------------------------------------------|
| Empirical formula               | C₇H₆N₂O₁₂                                |
| Formula weight                  | 1197.39                                  |
| Temperature                     | 170.00(13) K                             |
| Wavelength                      | 1.5418 Å                                 |
| Crystal system                  | monoclinic                               |
| Space group                     | P2₁                                      |
| Unit cell dimensions            | a = 20.0678(1) Å α = 90°                 |
|                                 | b = 15.8911(1) Å β = 108.962(1) °       |
|                                 | c = 25.6047(2) Å γ = 90°                |
| Volume                          | 7722.22(10) Å³                           |
| Z                               | 4                                        |
| Density (calculated)            | 1.030 g/cm³                              |
| Absorption coefficient          | 0.554 mm⁻¹                               |
| F(000)                          | 2548.0                                   |
| Crystal size                    | 0.2 × 0.1 × 0.05 mm³                     |
| Theta range for data collection | 4.656 to 150.874 °                      |
| Index ranges                    | -20 ≤ h ≤ 24, -19 ≤ k ≤ 19, -32 ≤ l ≤ 29 |
| Reflections collected           | 128124                                   |
| Independent reflections         | 30735 [R_{int} = 0.0425, R_{sigma} = 0.0349] |
| Completeness to theta =         | 75.437 99.99%                            |
| Absorption correction           | Multi-Scan                               |
Max. and min. transmission | 1.000 and 0.844  
Refinement method | Full-matrix least-squares on F^2  
Data / restraints / parameters | 30735/488/1665  
Goodness-of-fit on F^2 | 1.051  
Final R indices [I>2sigma(I)] | R_1 = 0.0636, wR_2 = 0.1867  
R indices (all data) | R_1 = 0.0692, wR_2 = 0.1945  
Extinction coefficient | n/a  
Largest diff. peak and hole | 0.54/-0.31 e.Å^3

**Figure S3.** ORTEP drawing of 1 with dihedral angles of biaryl moieties. Each unit cell contains two macrocycle molecules and one acetonitrile molecule in each cavity. The thermal ellipsoids are shown at a 50% probability.
3.2 CHON@1

Single crystals of CHON@1 suitable for X-ray crystallography were obtained by slow diffusion of Et₂O into a cyclohexanone solution of 1 at 4 °C. Crystallographic data were deposited at the Cambridge Crystallographic Data Center (CCDC 2067432).

| Table S5. Crystal data and structure refinement for CHON@1 |
|-----------------------------------------------------------|
| Empirical formula | C₈₁₀₆₅O₁₄ |
| Formula weight    | 1329.60    |
| Temperature       | 170.00(12) K |
| Wavelength        | 1.5418 Å   |
| Crystal system    | monoclinic |
| Space group       | P2₁       |
| Unit cell dimensions | a = 13.7152(1) Å, α = 90°  |
|                    | b = 15.9459(1) Å, β = 103.7111(1)°     |
|                    | c = 18.6299(2) Å, γ = 90°               |
| Volume            | 3958.28(5) Å³ |
| Z                 | 2         |
| Density (calculated) | 1.116 g/cm³ |
| Absorption coefficient | 0.600 mm⁻¹ |
| F(000)            | 1424.0    |
| Crystal size      | 0.32 × 0.06 × 0.05 mm³       |
| Theta range for data collection | 4.882 to 150.748 |
| Index ranges      | -16 ≤ h ≤ 17, -19 ≤ k ≤ 19, -23 ≤ l ≤ 20 |
| Reflections collected | 57056     |
| Independent reflections | 15673 [Rₑ = 0.0302, Rₛ = 0.0237] |
| Completeness to theta = 75.374° | 99.92% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 1.000 and 0.841 |
| Refinement method | Full-matrix least-squares on F² |
| Data / restraints / parameters | 15673/53/916 |
| Goodness-of-fit on F² | 1.036 |
| Final R indices [I>2sigma(I)] | R₁ = 0.0450, wR₂ = 0.1301 |
| R indices (all data) | R₁ = 0.0463, wR₂ = 0.1316 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.56/-0.25 e.Å⁻³ |
Figure S4. (a) ORTEP drawing of CHON@1 with dihedral angles of biaryl moieties. Each unit cell contains one macrocycle molecule, one Et₂O molecule outside the cavity, and one CHON molecule inside the macrocyclic cavity. The thermal ellipsoids shown at a 50% probability. (b) The top and side views of CHON@1 crystal structure before applying the SQUEEZE algorithm. The voids outside the macrocycle cavity are occupied by a diethyl ether and a disordered molecule (which cannot be well resolved, likely another Et₂O molecule) which are highlighted in yellow.
3.3 DFT computational analysis

The density functional theory method B3LYP functional with 6-31+G* basis set was used to fully optimize the structures, including CHON, CHOL, macrocycle 1, CHON@1 complex, and CHOL@1 complex. Then, the normal-mode analysis validated all stable points as the real minima. The binding energies of CHON@1 and CHOL@1 were defined as the single point energy at the B3LYP/6-311+G** level with the enthalpy correction at the B3LYP/6-31+G* level. At the same time, the dispersion correction with the Grimme’s D3 version was considered. All the calculations were performed with Gaussian 09 software package. Cartesian coordinates and corrected absolute energies of the optimized structures were listed in Table S6.

The calculated binding energies for CHON@1 and CHOL@1 are -114.2 and -102.4 kJ/mol, respectively.

Table S6. Cartesian coordinates (Å) and corrected absolute energies (hartree) of the optimized structures

| CHON        | -309.8348228 |
|-------------|--------------|
| O           | 2.29310100   | -0.00014800 | -0.36607000 |
| C           | 1.15558300   | -0.00010200 | 0.07393900  |
| C           | 0.39250800   | 1.28504300  | 0.36236600  |
| H           | 0.99238300   | 2.13543300  | 0.02428200  |
| H           | 0.27690900   | 1.36476000  | 1.45480800  |
| C           | -1.00941100  | 1.26609900  | -0.28716200 |
| H           | -0.89819900  | 1.30668100  | -1.38025500 |
| H           | -1.56175800  | 2.16728900  | 0.00658200  |
| C           | -1.78958600  | 0.00037800  | 0.09697900  |
| H           | -1.97636900  | 0.00071500  | 1.18180700  |
| H           | -2.77196300  | 0.00048300  | -0.39234100 |
| C           | -1.01012900  | -1.26598200 | -0.28660400 |
| H           | -0.89981500  | -1.30760600 | -1.37973000 |
| H           | -1.56272300  | -2.16662100 | 0.00839300  |
| C           | 0.39224700   | -1.28523000 | 0.36180700  |
| H           | 0.27765800   | -1.36570800 | 1.45432100  |
| H           | 0.99179600   | -2.13549100 | 0.02273200  |

| CHOL        | -311.0207149 |
|-------------|--------------|
| C           | -1.03714600  | 0.00000000  | -0.33181800 |
| C           | -0.33071500  | -1.26438100 | 0.17218800  |
| H           | -0.84429300  | -2.14847900 | -0.22452500 |
| H           | -0.42469200  | -1.30328000 | 1.27013800  |
| C           | 1.15964400   | -1.26817700 | -0.21058300 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| O    | 3.80527700 | -1.32103200 | -1.09396400 |
| H    | 3.66480300 | -2.16923200 | -1.55503400 |
| O    | 3.76551200 | 1.54211000  | 1.14199500  |
| H    | 3.57612900 | 2.39951600  | 1.56735000  |
| O    | 3.78265100 | 4.19817100  | 1.74378900  |
| O    | 0.59997900 | 5.50309200  | -2.60998000 |
| O    | -0.82803700 | 5.68730900  | 2.37517800  |
| O    | -3.83483200 | 3.92100700  | -1.93315300 |
| O    | -3.77357200 | 1.32789300  | -1.13061900 |
| H    | -3.60536600 | 2.17369300  | -1.59370100 |
| O    | -3.72062100 | -1.51492700 | 1.15672400  |
| H    | -3.53721000 | -2.36374600 | 1.60175100  |
| O    | -0.56599400 | -5.58075700 | 2.49876400  |
| O    | -3.74973200 | -4.15036400 | 1.81661500  |
| O    | 0.85237700  | -5.58660700 | 2.50012900  |
| O    | 3.95746800  | -3.94311400 | -1.79657700 |
| C    | 4.57125400  | -1.55640300 | 0.01563800  |
| C    | 4.48962800  | -2.75425000 | 0.76030900  |
| C    | 5.34592600  | -2.88367700 | 1.86349000  |
| H    | 5.32563800  | -3.81772000 | 2.42306100  |
| C    | 6.21897300  | -1.87352800 | 2.27352000  |
| C    | 7.11115000  | -2.10025500 | 3.48396700  |
| H    | 6.50895600  | -2.00416400 | 4.40177900  |
| H    | 7.48815100  | -3.13165100 | 3.47518800  |
| C    | 8.27584600  | -1.10570200 | 3.55673700  |
| H    | 8.80034100  | -1.20988500 | 4.51533400  |
| H    | 9.00557200  | -1.32992700 | 2.76434300  |
| C    | 7.74812400  | 0.32053900  | 3.36983300  |
| H    | 8.54701300  | 1.05911500  | 3.51469300  |
| H    | 6.98538700  | 0.52188300  | 4.13702400  |
| C    | 7.13240300  | 0.49152300  | 1.97519400  |

**RhombicArene (1) (-3769.088395)**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| O    | 3.80527700 | -1.32103200 | -1.09396400 |
| H    | 3.66480300 | -2.16923200 | -1.55503400 |
| O    | 3.76551200 | 1.54211000  | 1.14199500  |
| H    | 3.57612900 | 2.39951600  | 1.56735000  |
| O    | 3.78265100 | 4.19817100  | 1.74378900  |
| O    | 0.59997900 | 5.50309200  | -2.60998000 |
| O    | -0.82803700 | 5.68730900  | 2.37517800  |
| O    | -3.83483200 | 3.92100700  | -1.93315300 |
| O    | -3.77357200 | 1.32789300  | -1.13061900 |
| H    | -3.60536600 | 2.17369300  | -1.59370100 |
| O    | -3.72062100 | -1.51492700 | 1.15672400  |
| H    | -3.53721000 | -2.36374600 | 1.60175100  |
| O    | -0.56599400 | -5.58075700 | 2.49876400  |
| O    | -3.74973200 | -4.15036400 | 1.81661500  |
| O    | 0.85237700  | -5.58660700 | 2.50012900  |
| O    | 3.95746800  | -3.94311400 | -1.79657700 |
| C    | 4.57125400  | -1.55640300 | 0.01563800  |
| C    | 4.48962800  | -2.75425000 | 0.76030900  |
| C    | 5.34592600  | -2.88367700 | 1.86349000  |
| H    | 5.32563800  | -3.81772000 | 2.42306100  |
| C    | 6.21897300  | -1.87352800 | 2.27352000  |
| C    | 7.11115000  | -2.10025500 | 3.48396700  |
| H    | 6.50895600  | -2.00416400 | 4.40177900  |
| H    | 7.48815100  | -3.13165100 | 3.47518800  |
| C    | 8.27584600  | -1.10570200 | 3.55673700  |
| H    | 8.80034100  | -1.20988500 | 4.51533400  |
| H    | 9.00557200  | -1.32992700 | 2.76434300  |
| C    | 7.74812400  | 0.32053900  | 3.36983300  |
| H    | 8.54701300  | 1.05911500  | 3.51469300  |
| H    | 6.98538700  | 0.52188300  | 4.13702400  |
| C    | 7.13240300  | 0.49152300  | 1.97519400  |
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 6.57244200 | 1.43197500 | 1.92020000 |
| H    | 7.93916800 | 0.58628800 | 1.23103100 |
| C    | 6.22750400 | -0.65763300 | 1.56550900 |
| C    | 5.41238200 | -0.51334000 | 0.43013800 |
| C    | 5.40226400 | 0.75504600 | -0.36152200 |
| C    | 6.22033800 | -1.49322600 | 0.90485900 |
| H    | 6.50182200 | -1.03431100 | -2.33392700 |
| H    | 7.59584000 | -0.68442500 | -1.01773200 |
| C    | 8.20654000 | 1.16576400 | -2.92180800 |
| H    | 8.99486400 | 0.74381500 | -2.41633800 |
| H    | 8.68592800 | -0.73321800 | -3.33038100 |
| C    | 7.60157700 | 1.02275400 | -4.03867100 |
| H    | 6.78861400 | 0.46417500 | -4.52635000 |
| H    | 8.34857100 | 1.24558400 | -4.81160100 |
| C    | 7.05004900 | 2.32638500 | -3.44879900 |
| H    | 6.50515700 | 2.89447900 | -4.21471800 |
| H    | 7.89834200 | 2.96110500 | -3.14618100 |
| C    | 6.14846300 | 2.09065600 | -2.24803000 |
| C    | 5.22499800 | 3.06894300 | -1.87500100 |
| H    | 5.14896800 | 3.97451700 | -2.47484600 |
| C    | 4.37969600 | 2.93978400 | -0.76277400 |
| C    | 3.29026000 | 3.93625000 | -0.56080400 |
| C    | 2.98749600 | 4.55541500 | 0.66416800 |
| C    | 1.92285900 | 5.45291000 | 0.77284800 |
| H    | 1.66991400 | 5.89969800 | 1.72612200 |
| C    | 1.11703700 | 5.76458500 | -0.32430400 |
| C    | 1.42291000 | 5.16976200 | -1.56075100 |
| C    | 2.48939600 | 4.27589400 | -1.66622400 |
| H    | 2.70146100 | 3.78217400 | -2.60664900 |
| C    | 3.57564000 | 4.84238600 | 2.99585300 |
| H    | 4.33031500 | 4.42961600 | 3.66804000 |
| H    | 2.57376200 | 4.63296000 | 3.39403800 |
| H    | 3.71591500 | 5.92701500 | 2.90567200 |
| C    | 0.76729800 | 4.82624600 | -3.84800100 |
| H    | 0.64466000 | 3.74158900 | -3.72802800 |
| H    | 1.74952100 | 5.03739700 | -4.29270600 |
| H    | -0.01600500 | 5.21066200 | -4.50462400 |
| C    | -0.12717900 | 6.62181400 | -0.16100000 |
| H    | 0.00619900 | 7.30388400 | 0.68391800 |
| H    | -0.28772700 | 7.22434200 | -1.05957900 |
| C    | -1.33606900 | 5.73171000 | 0.07223500 |
| C    | -1.62799100 | 5.22759000 | 1.35690100 |
| C    | -2.64928700 | 4.29562200 | 1.54238300 |
| H    | -2.83204200 | 3.86659100 | 2.52006900 |
| C    | -3.42471600 | 3.82140700 | 0.46462500 |
| C    | -3.15100800 | 4.36364700 | -0.79842700 |
|   |   |   |   |
|---|---|---|---|
| C | -2.1292700 | 5.2945700 | -0.9865720 |
| H | -1.9265810 | 5.6469220 | -1.9924910 |
| C | -1.0224450 | 5.1687370 | 3.6832560 |
| H | -0.8530240 | 4.0838720 | 3.7123930 |
| H | -2.0303580 | 5.6703800 | 4.3141610 |
| C | -5.1867370 | 4.3918050 | -2.0582860 |
| H | -5.5829120 | 3.9411130 | -2.9711250 |
| H | -5.1942340 | 5.4853330 | -2.1469330 |
| H | -5.7919380 | 4.0822560 | -1.1989330 |
| C | -4.4410260 | 2.7665350 | 0.7309720 |
| C | -5.2922370 | 2.8972790 | 1.8388270 |
| H | -5.5829120 | 3.9411130 | -2.9711250 |
| H | -5.1942340 | 5.4853330 | -2.1469330 |
| H | -5.7919380 | 4.0822560 | -1.1989330 |
| C | -6.1636420 | 1.8889250 | 2.2541900 |
| H | -6.4469450 | 2.0199530 | 4.3828870 |
| H | -6.9124700 | 0.3023630 | 3.3580470 |
| H | -6.9282600 | -0.5029810 | 4.1250980 |
| H | -8.2176970 | 1.1245090 | 3.5430950 |
| H | -8.4948600 | 1.3481160 | 2.7514140 |
| H | -8.7405560 | 1.2308670 | 4.5022430 |
| C | -7.0518710 | 2.1173760 | 3.4671310 |
| H | -7.0765370 | -0.4770640 | 1.9634020 |
| H | -7.8833320 | -0.5748150 | 1.2196950 |
| H | -6.5161530 | -1.4172390 | 1.9113000 |
| C | -6.1729950 | 0.6712940 | 1.5481730 |
| C | -5.3611500 | 0.5244330 | 0.4111570 |
| C | -4.5232910 | 1.5675210 | -0.0143500 |
| C | -5.3472410 | -0.7515820 | -0.3677300 |
| C | -6.1572150 | -0.9159820 | -1.5027040 |
| C | -7.0561100 | 0.2264420 | -1.9433140 |
| H | -7.5220110 | 0.6935830 | -1.0672060 |
| H | -6.4163840 | 1.0056120 | -2.3863720 |
| C | -8.1289330 | -0.1903330 | -2.9579740 |
| H | -8.9240340 | -0.7527210 | -2.4456090 |
| H | -8.5997740 | 0.7036140 | -3.3871940 |
| C | -7.5229580 | -1.0728140 | -4.0543920 |
| H | -6.7039600 | -0.5288240 | -4.5481480 |
| H | -8.2672130 | -1.3057200 | -4.8268590 |
| C | -6.9832020 | -2.3684310 | -3.4365690 |
| H | -6.4370230 | -2.9536520 | -4.1884450 |
| H | -7.8370860 | -2.9924320 | -3.1275410 |
| C | -6.0878050 | -2.1160970 | -2.2345940 |
| C | -5.1739880 | -3.0935990 | -1.8364260 |
| H | -5.1018760 | -4.0113750 | -2.4178990 |
| C | -4.3335020 | -2.9487160 | -0.7223210 |
C  -4.46901900  -1.76762800  0.03955600
C  -3.25177600  -3.94760000  -0.49328400
C  -2.45147300  -4.32169400  -1.58823100
H   -2.66116100  -3.85275000  -2.54175200
C  -1.38747500  -5.21486500  -1.45664600
C  -1.08017200  -5.77129700  -0.20283300
C  -1.88758600  -5.42793000  0.88340600
H  -1.63402500  -5.84560500  1.84949300
C  -2.95237500  -4.53462000  0.74824700
C  -0.77690300  -4.98446500  -3.77022200
H  -0.01242500  -5.40591800  -4.42700500
H   -0.66048700  -3.89311200  -3.72415300
C   -1.77032300  -5.22869000  -4.17074100
C   -3.54142200  -4.75877500  3.08695000
H   -3.68032300  -5.84557600  3.02735900
H   -4.29681500  -4.32808800  3.74693300
C   -2.53987400  -4.53651300  3.47850600
C   -1.65421000  -6.61922300  -0.00698100
H   -0.32990000  -7.25314600  -0.88325900
H   -0.03090900  -7.27188700  -0.86061500
C    1.37025900  -5.71700200  0.20076300
C    2.15902000  -5.32099500  -0.88099200
H    1.92447100  -5.73562500  -1.85275300
C    3.18114400  -4.38001300  -0.73368600
C    3.45543700  -3.79880600  0.51656700
C    2.67625600  -4.22752700  1.60667900
H    2.86728300  -3.76500800  2.56729800
C    1.65404600  -5.16663100  1.46256600
C    3.77255900  -4.53724400  -3.07710200
H    3.96194700  -5.61742000  -3.03848100
H    4.50465400  -4.05992200  -3.73122300
H    2.76032500  -4.35436300  -3.46156800
C    1.05016000  -5.01444300  3.78449300
H    2.05762100  -5.22438300  4.16908800
H    0.31199200  -5.48612100  4.43728100
H    0.88514700  -3.92842700  3.76865800
C    4.51817400  1.77482400  0.02290500

CHON1  (-4077.966734)
  O  -3.55265300  -1.29943100  1.08599400
  H  -3.56072800  -2.14858100  1.56955200
  O  -3.36457700  1.73136500  -1.00751400
  H  -3.23061500  2.59714000  -1.43752000
  O  -3.58379100  4.38910400  -1.55973800
  O  -0.33896600  5.77760700  2.72081100
  O  0.83298700  5.96339500  -2.31351200
  O  3.89332500  4.03914000  1.88833400

S16
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| O    | 3.53229900 | 1.45244100 | 1.16246300 |
| H    | 3.48073000 | 2.31476000 | 1.62315200 |
| O    | 3.17844000 | -1.44456800| -0.88731600|
| H    | 2.90826100 | -2.26432600| -1.34131400|
| O    | 0.34358800 | -5.76244900| 2.66324800 |
| O    | 3.39030700 | -4.06150900| -1.64943000|
| O    | -0.93725000| -5.78010100| -2.42482500|
| O    | -4.03432700| -3.86808700| 1.76535800 |
| C    | -4.33186900| -1.44300300| -0.03591100|
| C    | -4.34269600| -2.62833400| -0.80136900|
| C    | -5.16896000| -2.65421300| -1.93339300|
| H    | -5.21578800| -3.57316000| -2.51547200|
| C    | -5.93114600| -1.55773600| -2.34387400|
| C    | -6.78877400| -1.67102100| -3.59411100|
| C    | -6.14316500| -1.58743300| -4.48302900|
| H    | -7.24069900| -2.67065800| -3.64045400|
| C    | -7.87235900| -0.58907200| -3.67121600|
| H    | -8.36431400| -0.61827300| -4.65189100|
| H    | -8.64762600| -0.78554200| -2.91562900|
| C    | -7.24745600| 0.78513000  | -3.40916500 |
| H    | -7.98277500| 1.58722000  | -3.55284000 |
| H    | -6.44273100| 0.95546200  | -4.14011400 |
| C    | -6.67389300| 0.85796100  | -1.98807800 |
| H    | -6.05242400| 1.75354700  | -1.87694400 |
| H    | -7.49838800| 0.98036300  | -1.26793600 |
| C    | -5.86800600| -0.36850100| -1.59560100 |
| C    | -5.08080300| -0.32802100| -0.43096800 |
| C    | -5.03955200| 0.89146200  | 0.42975700  |
| C    | -5.86238100| 0.98688900  | 1.56966000  |
| C    | -6.78778100| -0.16793100| 1.90898300 |
| H    | -6.17015800| -0.99926000| 2.28227700 |
| H    | -7.26259800| -0.54789200| 0.99647300 |
| C    | -7.85355600| 0.18608100  | 2.95415200  |
| H    | -8.63772400| 0.80279700  | 2.48993600 |
| H    | -8.34092700| -0.73077700| 3.30979800 |
| C    | -7.23216800| 0.96677400  | 4.11685000 |
| H    | -6.41938700| 0.37281800  | 4.56097900 |
| H    | -7.97004000| 1.14723400  | 4.90917200 |
| C    | -6.67536000| 2.29977100  | 3.60292000 |
| H    | -6.11728400| 2.81483300  | 4.39626200 |
| H    | -7.52026000| 2.95951600  | 3.34876800 |
| C    | -5.78702100| 2.13095800  | 2.38095700 |
| C    | -4.87853700| 3.13665600  | 2.04457800 |
| H    | -4.81543300| 4.02071700  | 2.67706400 |
| C    | -4.03876500| 3.06367900  | 0.92424300 |
| C    | -3.00384000| 4.11252300  | 0.72263900 |
| C    | -2.78026800| 4.77471800  | -0.49635100|
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -1.77485000 | 5.73514000 | -0.61679500 |
| H       | -1.57567500 | 6.21209600 | -1.56773400 |
| C       | -0.94796100 | 6.06194300 | 0.45995900 |
| C       | -1.18013000 | 5.42682200 | 1.69298900 |
| H       | -2.34666700 | 3.94760000 | 2.74641900 |
| C       | -3.47322800 | 5.08597000 | -2.79604300 |
| H       | -4.22646200 | 4.64470500 | -3.45150800 |
| C       | -2.47768200 | 4.95788800 | -3.32416760 |
| H       | -3.68102700 | 6.15504200 | -2.66235900 |
| C       | -0.41337500 | 5.05073200 | 3.93969900 |
| H       | -0.23529700 | 3.97964200 | 3.77539800 |
| H       | 0.37521400  | 5.45738400 | 4.57617500 |
| C       | 0.28194800  | 6.93094100 | 0.25279400 |
| H       | 0.11686200  | 7.61811800 | -0.58194100 |
| H       | 0.48975800  | 7.52347700 | 1.14783600 |
| C       | 1.45246200  | 6.00643800 | -0.03629800 |
| C       | 1.64206300  | 5.46081500 | -1.32363000 |
| C       | 2.57015500  | 4.44227000 | -1.53464900 |
| H       | 2.66628600  | 3.97853000 | -2.50879800 |
| C       | 3.35155800  | 3.92372900 | -0.48283900 |
| C       | 3.19486200  | 4.51638500 | 0.77723100 |
| C       | 2.26465100  | 5.53259600 | 0.99188600 |
| H       | 2.13680200  | 5.91483300 | 1.99900400 |
| C       | 0.89020900  | 5.37429900 | -3.60500600 |
| H       | 0.62806900  | 4.30812500 | -3.56894100 |
| H       | 1.88409200  | 5.49046200 | -4.05781300 |
| H       | 0.15610800  | 5.91185100 | -4.20941700 |
| C       | 5.28783700  | 4.38536000 | 1.93366700 |
| H       | 5.68800800  | 3.91932000 | 2.83693600 |
| H       | 5.39896900  | 5.47511800 | 1.99330800 |
| H       | 5.81626400  | 4.00228100 | 1.05371300 |
| C       | 4.25131500  | 2.77540400 | -0.76569600 |
| C       | 5.05452300  | 2.79879500 | -1.91565100 |
| H       | 5.08242400  | 3.71390500 | -2.50543800 |
| C       | 5.81871200  | 1.70791900 | -2.33278000 |
| C       | 6.65329600  | 1.81816000 | -3.59876600 |
| H       | 5.99234400  | 1.72844100 | -4.47567900 |
| H       | 7.10177100  | 2.81886200 | -3.65770300 |
| C       | 7.73715200  | 0.73773500 | -3.68967700 |
| H       | 8.52389000  | 0.93725500 | -2.94675600 |
| H       | 8.21359100  | 0.76500300 | -4.67799300 |
| C       | 7.11663900  | -0.63571600 | -3.41429800 |
| H       | 6.29991400  | -0.80763600 | -4.13111800 |
| H       | 7.84877500  | -1.43843300 | -3.56870700 |
| C       | 6.56695800  | -0.70695100 | -1.98377600 |
| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| H       | 7.401836 | -0.836452 | -1.277025 |
| H       | 5.942334 | -1.599088 | -1.863468 |
| C       | 5.774811 | 0.523286  | -1.574876 |
| C       | 5.015263 | 0.487006  | -0.392308 |
| C       | 4.269123 | 1.599808  | 0.018380  |
| C       | 4.982920 | -0.747644 | 0.446693  |
| C       | 5.871922 | -0.912719 | 1.521438  |
| C       | 6.355070 | 0.209841  | 1.866222  |
| H       | 7.254369 | 0.637703  | 0.947195  |
| H       | 6.255334 | 1.022470  | 2.330915  |
| C       | 7.963482 | -0.217573 | 2.814107  |
| H       | 8.701830 | -0.818764 | 2.265810  |
| H       | 8.491833 | 0.670138  | 3.185494  |
| C       | 7.408541 | -1.052153 | 3.973157  |
| H       | 6.642794 | -0.469464 | 4.506770  |
| H       | 8.196793 | -1.289551 | 4.699207  |
| C       | 6.787925 | -2.345128 | 3.429717  |
| H       | 6.272260 | -2.889417 | 4.232151  |
| H       | 7.598625 | -3.007308 | 3.086181  |
| C       | 5.825178 | -2.096397 | 2.279600  |
| C       | 4.883761 | -3.072196 | 1.944273  |
| H       | 4.852022 | -3.992633 | 2.525301  |
| C       | 3.973205 | -2.927086 | 0.888095  |
| C       | 4.043146 | -1.738228 | 0.131081  |
| C       | 2.933276 | -3.967335 | 0.671795  |
| C       | 2.175573 | -4.410982 | 1.770087  |
| H       | 2.373436 | -3.951245 | 2.730976  |
| C       | 1.154630 | -5.351740 | 1.626898  |
| C       | 0.874863 | -5.903260 | 0.364170  |
| C       | 1.651197 | -5.494973 | 0.720853  |
| H       | 1.405033 | -5.896213 | -1.694147 |
| C       | 2.652260 | -4.533657 | -0.583261 |
| C       | 0.522281 | -5.163670 | 3.937387  |
| H       | -0.227782 | -5.618396 | 4.588774  |
| H       | 0.362480 | -4.077119 | 3.895239  |
| H       | 1.522574 | -5.367520 | 4.343656  |
| C       | 3.024825 | -4.469475 | -2.968605 |
| H       | 3.176118 | -5.548470 | -3.101484 |
| H       | 3.695758 | -3.924645 | -3.635626 |
| H       | 1.986112 | -4.195599 | -3.180746 |
| C       | -0.351779 | -6.771418 | 0.134636  |
| H       | -0.557855 | -7.387808 | 1.013846  |
| H       | -0.181648 | -7.436397 | -0.716561 |
| C       | -1.525209 | -5.845924 | -0.138484 |
| C       | -2.318687 | -5.386439 | 0.914371  |
| H       | -2.138241 | -5.802392 | 1.897845  |
| C       | -3.259592 | -4.372659 | 0.728444  |
| Atom | X-Position | Y-Position | Z-Position |
|------|------------|------------|------------|
| H    | 4.48214800 | 4.76981000 | 3.39810100 |
| H    | 2.70480900 | 4.93113300 | 3.27009100 |
| H    | 3.77437800 | 6.20276600 | 2.59432600 |
| C    | 0.10400400 | -3.66385100| -0.36385100|
| H    | 0.01762800 | 3.35124800 | -3.34338600|
| H    | 0.99510700 | 4.51842300 | -4.29482500|
| H    | -0.78259900| 4.67848100 | -4.23624200|
| C    | -0.35428700| 6.60954200 | 0.13338700 |
| H    | -0.18475900| 4.16120700 | 1.60584500 |
| C    | -2.80285200| 3.65339300 | 2.55854200 |
| C    | -3.57591500| 3.75897000 | 0.56743000 |
| C    | -4.48214800| 4.76981000 | 3.39810100 |
| H    | -2.32154600| 5.77720000 | -1.87039500|
| C    | -0.78335200| 4.75852100 | 3.58297200 |
| H    | -0.59693300| 3.69203000 | 3.39846500 |
| H    | -1.71498100| 4.87635400 | 4.15255700 |
| H    | -5.56005300| 4.42831800 | -1.75659700|
| C    | -6.01357200| 4.03047400 | -2.66732800|
| H    | -5.61447000| 5.52401200 | -1.87039500|
| H    | -6.08001400| 4.02978300 | -0.87844100|
| C    | -4.52970100| 2.64986400 | 0.83040300 |
| C    | -3.09672000| 2.66172900 | 1.99525500 |
| H    | -5.29641300| 3.55790200 | 2.61411900 |
| C    | -6.09650300| 1.57865700 | 2.39303800 |
| H    | -6.91297200| 1.67748600 | 3.67201600 |
| H    | -6.24075900| 1.56924900 | 4.53823100 |
| H    | -7.35142600| 2.68108900 | 3.75211800 |
| C    | -8.00606200| 0.60645400 | 3.76272100 |
| H    | -8.80310700| 0.82653300 | 3.03688700 |
| H    | -8.46556200| 0.62141400 | 4.75927500 |
| C    | -7.40522800| -0.76845600| 3.45309400 |
| H    | -6.57736500| -0.96087800| 4.15187700 |
| H    | -8.14336000| -1.56592400| 3.60694900 |
| C    | -6.88199100| -0.81949000| 2.01183500 |
| H    | -7.73180600| -0.92316700| 1.31887000 |
| H    | -6.27172700| -1.71704700| 1.86404400 |
| C    | -6.08006700| 0.40746500 | 1.61286600 |
| C    | -5.33661100| 0.38074400 | 0.42226700 |
| C    | -4.59368800| 1.49954900 | 0.01410800 |
| C    | -5.24694500| -0.85012600| -0.41853700|
| C    | -6.01500300| -0.99888700| -1.58486300|
C  -6.97325600  0.10882000  -1.98554700
H  -7.49535200  0.48718800  -1.09803100
H  -6.37233500  0.95305600  -2.35698900
C  -7.98331000  -0.31123800  -3.06094400
H  -8.75456600  -0.95651200  -2.61428000
H  -8.49915800  0.57554100  -3.45142300
C  -7.28247700  -1.07975500  -4.18665100
H  -6.48411500  -0.45346000  -4.61155000
H  -7.98174500  -1.30815200  -5.00124000
C  -6.68056700  -2.37637800  -3.63124900
H  -6.06906400  -2.87412500  -4.39566100
H  -7.50113200  -3.07353000  -3.39768800
C  -5.84806100  -2.14720400  -2.38030400
C  -4.89687500  -3.09708300  -2.00030400
H  -4.75615600  -3.97880200  -2.62340100
C  -4.10719700  -2.96763000  -0.84910100
C  -3.01093400  -3.94073900  -0.59755500
C  -2.12538900  -4.24013100  -1.64663300
H  -2.27330200  -3.72386200  -2.58732800
C  -1.05482700  -5.11854900  -1.47742900
C  -0.83944100  -5.74293900  -0.23656500
C  -1.73055600  -5.46857000  0.80222800
H  -1.54233500  -5.93242300  1.76185300
C  -2.79168200  -4.57864200  0.63492000
C  -0.18248900  -4.63848300  -3.66194100
H  0.66823400  -4.97480600  -4.25944300
H  -0.10117300  -3.56599500  -3.44727600
H  -1.10819800  -4.81275900  -4.22724300
C  -3.52706300  -4.89797700  2.92033000
H  -3.65146800  -5.98278600  2.81316900
H  -4.32625200  -4.49743000  3.54685300
H  -2.55419100  -4.68175500  3.38047500
C  0.40264600  -6.57982300  0.01459400
H  0.61276400  -7.21703000  -0.84998600
H  0.23494800  -7.22919800  0.87921900
C  1.58416200  -5.66025100  0.26758400
C  2.45374900  -5.32145000  -0.77187100
H  2.30249100  -5.79912700  -1.73146300
C  3.43639000  -4.34575100  -0.60656000
C  3.60076000  -3.69148500  0.62595100
C  2.75106100  -4.06711600  1.67749700
H  2.85203900  -3.54094400  2.61862100
C  1.74653800  -5.02046400  1.50799700
C  4.20328400  -4.60390400  -2.88831800
H  4.42967800  -5.67076000  -2.76746900
H  4.96430200  -4.13624200  -3.51600700
| Atoms | x | y | z |
|-------|---|---|---|
| C     | 3.21721500 | -4.48902500 | -3.35816400 |
| H     | 0.75820500  | -4.50292000  | 3.63242100  |
| H     | 1.65326100  | -4.57919900  | 4.26511200  |
| H     | -0.10313300 | -4.86542000  | 4.19936000  |
| C     | 4.41919000  | 1.89336600   | -0.05395600 |
| C     | 0.01353000  | -0.70502200  | 1.02067100  |
| C     | 0.12820800  | -1.32484900  | -0.37716500 |
| H     | 1.17779700  | -1.25609000  | -0.70286200 |
| H     | -0.12796200 | -2.39039000  | -0.32105200 |
| C     | -0.77700800 | -0.59439600  | -1.38484400 |
| H     | -1.82933500 | -0.73699400  | -1.10603200 |
| H     | -0.65302600 | -1.03490400  | -2.38473000 |
| C     | -0.47197600 | 0.91257600   | -1.42050100 |
| H     | 0.54965600  | 1.07198700   | -1.79940600 |
| H     | -1.16182200 | 1.41687900   | -2.11019000 |
| C     | -0.59087300 | 1.53149600   | -0.01954000 |
| H     | -1.63689100 | 1.46607600   | 0.30618700  |
| H     | -0.33523400 | 2.59921600   | -0.04988000 |
| C     | 0.31253700  | 0.79956800   | 0.98764800  |
| H     | 1.36800500  | 0.94362800   | 0.71591500  |
| H     | 0.18506400  | 1.21189600   | 1.99825500  |
| H     | -1.00486100 | -0.86457600  | 1.39550100  |
| O     | 0.85940200  | -1.38799000  | 1.96715700  |
| H     | 1.77420700  | -1.33097900  | 1.64180300  |
IV. Vapor Sorption Experiments

4.1 Preparation of the activated crystals of 1

(1) Crystallization by diffusion of MeOH into a solution of 1 in mixed CHCl₃/MeCN (1:3) at 25 °C;
(2) Heating under vacuum (ca. 200 Pa) at 50 °C for 5 hours;
(3) The resulting white powder was cooled to room temperature, and can be stored in a capped vial in air under room temperature for at least one month.

Figure S5. N₂ adsorption isotherm (at 77 K) of activated 1. The low BET surface area (<5 m²/g) indicates that the activated 1 is essentially nonporous.

4.2 Single-component vapor adsorption procedures

(1) The activated crystals of 1 (1-10 mg) were added to a 4 mL uncapped glass vial, and the vial was carefully transferred into a 20 mL vial containing CHON or CHOL (0.2 mL);
(2) The 20 mL vial was sealed with a teflon-lined septum cap and placed in an oven (preheated at 30 °C);
(3) At each time point, the powder sample was quickly taken out of the vial using a spatula, and was placed in an oven in air at 40 °C for 1 h prior to NMR (Figures 3a and S6), PXRD (Figures 3b and S7), TGA (Figures S8, S9 and S10), or IR analysis (Figure S11).
Figure S6. $^1$H NMR spectra (400 MHz, CDCl$_3$, 298 K) of (a) activated 1; (b) pure CHOL; (c) activated 1 after treatment with CHOL vapor at 30 °C for 24 h; (d) pure CHON; (e) activated 1 after treatment with CHON vapor at 30 °C for 3 h; (f) ground amorphous 1 after treatment with CHON vapor at 30 °C for 3 h.

Notes: The noncovalent interactions between 1 and CHON in solution are not strong enough to be observed by NMR. No CHON adsorption was observed with ground amorphous powder of 1.
Notes: A new peak appears around 12 in the PXRD pattern after treatment with CHOL vapor. Our current rationale is that the macrocycle 1 is found slightly soluble in liquid CHOL (about 1 milligram per mL). Hence, although CHOL vapor cannot be adsorbed into the activated NACs of 1, the CHOL vapor may “solvate” the surface of solid 1, leading to minor changes of the crystalline state of 1. Nonetheless, the most part of the PXRD pattern after treatment with CHOL vapor matches with that of the activated 1.

**Figure S7.** PXRD patterns of 1 under different conditions.

**Figure S8.** TGA of the activated crystals of 1, showing good thermal stability below 190 °C, and 2.8% weight loss from 50 °C to 300 °C.
Figure S9. TGA of the activated crystals of 1 after CHON adsorption at 30 °C for 30 min, showing 20.3% weight loss from 50 °C to 300 °C.

Notes: Suppose that the 20.3% weight loss in Figure S8 consists of the CHON desorption and the intrinsic weight loss of 1 observed in Figure S8. The molar ratio of the adsorbed CHON relative to 1 can be calculated based on the following equation (molecular weight: 1157.4 for 1, and 98.1 for CHON), and the result matches with the amount of adsorbed CHON measured by NMR (Figure 3a in the manuscript).

\[
\frac{1157.4 \times (1 - 2.8\%) - 1157.4}{1 - 20.3\%} = \frac{2.59 \text{ equiv.}}{98.1}
\]

Figure S10. TGA of the activated crystals of 1 after CHOL adsorption at 30 °C for 30 min, indicating minimal CHOL adsorption based on the 2.8% weight loss from 50 °C to 300 °C.
Figure S11. IR analysis of macrocycle 1 and CHON. Consistent with Brønsted acid interaction, the C=O stretching band moved from 1713 cm\(^{-1}\) for CHON to 1703 cm\(^{-1}\) when adsorbed by 1.

4.3 Mixed vapor adsorption procedures

(1) The activated crystals of 1 (1-10 mg) were added to a 4 mL uncapped glass vial, and the vial was carefully transferred into a 20 mL vial containing mixed CHON (0.1 mL) and CHOL (0.1 mL);
(2) The 20 mL vial was sealed with a teflon-lined septum cap and placed in an oven (preheated at 30 °C);
(3) At each time point, the powder sample was quickly taken out of the vial using a spatula, and was placed in an oven in air at 40 °C for 1 h prior to NMR (Figures 4c and S12), PXRD (Figures S13 and S14), or GC analysis (Figures 4b and S15);
(4) (Reactivation for recycling experiments, optional), powder 1 after vapor adsorption was heated under vacuum (ca. 200 Pa) at 100 °C for 12 hours, and was cooled to room temperature under vacuum prior to the next cycle.
Figure S12. Time-dependent selective adsorption plot of mixed vapor (CHOL and CHON) employing 1 at 30 °C.

Figure S13. PXRD patterns of 1 after vapor adsorption at 30 °C for 30 min.

Figure S14. PXRD patterns of (I) activated 1 and (II) re-activated 1 after adsorption-recycling experiments.
Figure S15. GC analysis of (a) pure CHOL; (b) pure CHON; (c) V/V 1:1 mixture of liquid CHOL/CHON, verifying almost identical GC response factors of CHOL and CHON; (d) the adsorbed CHOL/CHON by activated 1 (after adsorption of mixed vapor at 30 °C for 30 min).

Notes: The GC method was as follows: the oven was initially programmed at 50 °C for 3 min, then ramped at 10 °C/min increments to 120 °C, followed by a temperature increase to 300 °C at a rate of 25°C/min. Each test sample was dissolved in CH₂Cl₂ in a 2-mL vial prior to analysis.
Figure S16. HPLC analysis of (a) a mixed sample of (S,S)-1 and (R,R)-1; (b) activated (S,S)-1; (c) (S,S)-1 after recycled 5 times.

Notes: The HPLC method was as follows: CHIRALPAK® OD-H column using 98:2 hexane-iPrOH as mobile phase, with a flow rate of 1.0 mL/min. The above results indicated no racemization, confirming the thermal stability of 1.
Notes: Vapor pressures were calculated according to the Antoine equation,
\[
\ln(P/kPa) = A - \frac{B}{(T/K)} + C
\]
The Antoine constants were fitted based on the reported data in Tables S7 and S8 (ref. 16a in the manuscript) using a linear regression method (ref. 16b in the manuscript).

### Table S7. Vapor Pressures of CHON

| Temp (°C) | 1.4 | 26.4 | 38.7 | 52.5 | 67.8 | 77.5 | 90.4 | 110.3 | 132.5 | 155.6 |
|-----------|-----|------|------|------|------|------|------|-------|-------|-------|
| Temp (K)  | 274.55 | 299.55 | 311.85 | 325.65 | 340.95 | 350.65 | 363.55 | 383.45 | 405.65 | 428.75 |
| Vapor Pressure (mmHg) | 1 | 5 | 10 | 20 | 40 | 60 | 100 | 200 | 400 | 760 |
| Vapor Pressure (kPa) | 0.1333 | 0.6665 | 1.333 | 2.666 | 5.332 | 7.998 | 13.33 | 26.66 | 53.32 | 101.31 |

### Table S8. Vapor Pressures of CHOL

| Temp (°C) | 21 | 44 | 56 | 68.8 | 83 | 91.8 | 103.7 | 121.7 | 141.4 | 161 |
|-----------|----|----|----|------|----|------|-------|-------|-------|-----|
| Temp (K)  | 294.15 | 317.15 | 329.15 | 341.95 | 356.15 | 364.95 | 376.85 | 394.85 | 414.55 | 434.15 |
| Vapor Pressure (mmHg) | 1 | 5 | 10 | 20 | 40 | 60 | 100 | 200 | 400 | 760 |
| Vapor Pressure (kPa) | 0.1333 | 0.6665 | 1.333 | 2.666 | 5.332 | 7.998 | 13.33 | 26.66 | 53.32 | 101.31 |

### Table S9. Calculated Antoine constants for CHON and CHOL

|         | A    | B     | C      |
|---------|------|-------|--------|
| CHON    | 14.649 | 3889.3 | -41.149 |
| CHOL    | 15.849 | 4259.5 | -55.510 |

At 30°C (303.15 K), calculated \(P(\text{CHON}) = 0.82\ kPa; P(\text{CHOL}) = 0.25\ kPa

Figure S17. Vapor pressure-T curves based on calculated Antoine constants: (a) CHON, (b) CHOL.
4.4 Purity enhancement of liquid CHOL using solid-vapor adsorption

(1) A sample of 98:2 CHOL/CHON was prepared by mixing 8 μL of CHON and 392 μL of CHOL. The CHOL content was confirmed by GC analysis as 98.1%;
(2) A 4 mL vial containing the activated crystals of 1 was placed in a 20 mL vial containing the 98:2 CHON/CHOL mixture (50 μL);
(3) The 20 mL vial was sealed with a teflon-lined septum cap and placed in an oven (preheated at 30 °C);
(4) After 30 min, the liquid in the 20 mL vial was analyzed by GC.

**Table S10.** Evaluation of quantity of 1 for the purity enhancement of liquid CHOL.

| entry | quantity of 1 used (mg) | purity of CHOL after solid-vapor adsorption |
|-------|-------------------------|-------------------------------------------|
| 1     | 3                       | 98.7%                                     |
| 2     | 6                       | 99.6%                                     |
| 3     | 9                       | 99.7%                                     |

**Figure S18.** GC analysis of (a) the sample of 98:2 CHOL/CHON; (b) the liquid after vapor adsorption by 1 (3 mg); (c) the liquid after vapor adsorption by 1 (6 mg); and (d) the liquid after vapor adsorption by 1 (9 mg). All vapor adsorptions were conducted at 30 °C for 30 min. The GC method was identical to Figure S14.
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