

Supporting Information for

Selective Separation of Branched Alkane Vapor by

Thiacalixarene Supramolecular Crystals Having Shape-

Recognition Properties

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Table of Contents

1. Experimental Section

Materials

Methods

Solution ^1H NMR

Powder X-ray diffraction

Growth of isooctane included single crystals of $1 \cdot$ isooctane ($1 \cdot iso-C_8$)

X-Ray Crystallography

Crystallographic Data

Table S1. Experimental single crystal X-ray data for $1 \cdot iso-C_8$.

Vapor sorption measurement of the activated crystal 1α toward isooctane and n -heptane

Thermogravimetric analysis (TGA)

Gas chromatography with head-space method

2. Supporting figures

Figure S1 Sorption experiments of single or two-component alkane vapors by the activated crystal 1α for isooctane ($iso-C_8$) and n -heptane ($n-C_7$) in vials.

Figure S2 ^1H NMR spectrum after the activated crystal 1α exposed to $iso-C_8$ vapor.

Figure S3 PXRD patterns of as-synthesized $1 \cdot CyC_6$ (black, solid line) and the activated crystal 1α exposed to $iso-C_8$ vapor in vials (red, dotted line).

Figure S4 PXRD patterns of as-synthesized $1 \cdot iso-C_8$ (black, solid line) and the activated crystal 1α exposed to $iso-C_8$ vapor in vials (red, dotted line).

Figure S5 An asymmetrical unit of single crystal $1 \cdot iso-C_8$ was comprised by three thiacalixarene molecules (stick models) and three disordered isooctane molecules (space filling model). Propyl moieties as a partial of three thiacalixarenes were disordered and the disordered parts were shown by gray and white circles around propyl moieties.

Figure S6 Projection of intermolecular S-H hydrogen bonding (green dotted lines) and S- π (purple dotted line) interactions supporting formation of a 1D preorganized

channel-like void of $\mathbf{1} \cdot iso-C_8$ assembling by S- π interactions and S-H hydrogen bonding.

Figure S7 Projection of intermolecular Br-H (light blue dotted line) contacts supporting formation of pillar units in the 1D channel-like structure of $\mathbf{1} \cdot iso-C_8$.

Figure S8 Projection of the void sizes and the assembly size of the two extended structures of a) $\mathbf{1} \cdot CyC_6$ and b) $\mathbf{1} \cdot iso-C_8$.

Figure S9 Time-dependent quantity adsorbed of *iso-C*₈ vapor by $\mathbf{1a}$.

Figure S10 Sorption isotherms of *iso-C*₈ vapor at 25 °C of the activated crystal $\mathbf{1a}$ at the 1st cycle (red circles) and the re-activated crystal $\mathbf{1a}$ at the 2^{ed} – 5th cycles (blue, green, yellow, and pink circles).

Figure S11 PXRD patterns of the activated crystal $\mathbf{1a}$ (black, solid line) and the re-activated crystal $\mathbf{1a}$ after 5th sorption-desorption cycle (red, dotted line).

Figure S12 Heating curves of differential scanning calorimetry (DSC) of the $\mathbf{1a}$ adsorbed *iso-C*₈.

Figure S13 Thermogravimetric analysis (TGA) of the $\mathbf{1a}$ adsorbed *iso-C*₈.

Figure S14 Change in quantity adsorbed of *iso-C*₈ over time when $\mathbf{1a}$ is exposed to *iso-C*₈/*n-C*₇ mixed system with different composition (*iso-C*₈:*n-C*₇ = 0.2:1–0.8:1).

Figure S15 ¹H NMR spectra after $\mathbf{1a}$ exposed *iso-C*₈/*n-C*₇ mixed system at various compositions of *iso-C*₈ : *n-C*₇ = 0.2:1, 0.4:1, 0.6:1, and 0.8:1 for 48 h..

Figure S16 Gas chromatograms by head-space method for *iso-C*₈/*n-C*₇ ratio in $\mathbf{1a}$ which exposed *iso-C*₈/*n-C*₇ mixed system at various compositions of *iso-C*₈ : *n-C*₇ = a) 0.2:1, b) 0.4:1, c) 0.6:1, and d) 0.8:1 for 48 h.

Figure S17 Gas-chromatographic analysis of RON upon the exposure of *iso-C*₈/*n-C*₇ mixed vapors (*iso-C*₈:*n-C*₇ ratio = 0.2:1–0.8:1) to activated crystal $\mathbf{1a}$.

3. References

1. Experimental Section

Materials

All solvents were purchased from commercial sources, and used as received. The reactions were carried out in nitrogen atmosphere. *p*-Bromothiacalix[4]arene propyl ether molecules as a 1,3-alternate conformer was also synthesized according to the literature.^{S1, S2}

The synthetic method and ¹H NMR data of *p*-bromothiacalix[4]arene propyl ether molecules as a 1,3-alternate conformer are shown below for reference

To a suspended solution of *p*-bromothiacalix[4]arene (0.5 g, 0.616 mmol) in acetone (50 mL) and potassium carbonate (0.675 g, 0.488 mmol) was added. 1-iodopropane (1 mL, 10.3 mmol) was added to the solution, and then, the reflux was maintained for 48 h under nitrogen atmosphere. After cooling to the ambient temperature, the solvent was evaporated to dryness. The powder was dissolved in CHCl₃ (50 mL) and treated with 1M HCl (50 mL) and water (2×50 mL). The organic phase was dried over non-hydrous Na₂SO₄ and concentrated under reduced pressure, washed with methanol and filtered. A solid was included two components, *p*-bromothiacalix[4]arene propyl ether as a 1,3-alternate and a partial cone conformers. Treatment of the solid mixture of two conformation isomers with cyclohexane/CHCl₃ produces crystals of **1**·CyC₆ directly by crystallization and a filtrate, which is dried and then treated with CCl₄ to produce crystals of *p*-bromothiacalix[4]arene propyl ether as the partial cone conformer with CCl₄ upon

crystallization. Crystallization solvent free **1** was prepared by heating at 100 °C *in vacuo* overnight.

Preliminary data for **1**: ¹H NMR (500 MHz, CDCl₃, δ from TMS): δ 7.51 [8H, s, Ar-H], 3.88 [8H, t, *J* = 7.1, -O-CH₂-CH₂-CH₃], 1.35 [8H, m, -O-CH₂-CH₂-CH₃], 0.77 [12H, t, *J* = 7.7, -O-CH₂-CH₂-CH₃]; ¹³C NMR (125 MHz, CDCl₃, δ from TMS): δ 9.96, 22.56, 71.29, 114.84, 130.02, 134.78, 159.01.

Methods

Solution ¹H NMR

Solution ¹H NMR spectra were recorded at 500 MHz JEOL ECA500 instrument. Chemical shifts are quoted as parts per million (ppm) relative to tetramethylsilane (CDCl₃).

Powder X-ray diffraction

Powder X-ray diffractions (PXRD) were collected with a Rigaku Ultima IV diffractometer by using Cu Kα radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA) with a graphite monochromator at a step width of 0.02° 2θ and a scan speed 2.000° min⁻¹.

Growth of isooctane included single crystals of **1**·isooctane (**1**·*iso*-C₈)

300 mg of the activated **1a** were dissolved in chloroform 3 mL into vial. 3 mL of isooctane was added on the chloroform solution. The resultant solutions was allowed to slowly evaporate at room temperature over 1 day to afford colorless large crystals. The resultant crystals were conducted for analysis of single-crystal diffraction, PXRD, and NMR studies.

X-Ray Crystallography

Single crystals of **1-iso-C₈** suitable for single-crystal X-ray diffraction studies were formed. The crystals in mother liquid were picked up with a pipette, and dropped in paraton oil. The single crystals coated with oil were isolated on MicroMounts, and the crystals were immediately placed in a cold nitrogen stream. X-Ray diffraction data for **1-isooctane** were collected on a Rigaku XtaLaB P200 with graphite-monochromated Mo K α radiation. The structures were solved by direct methods using SHELXT (Version 2014)^{S3} and refined using the full-matrix least-squares method on F^2 using the SHELXL (Version 2014)^{S4} Program. All materials for publication were prepared by Yadokari XG software ^{S5,S6}. All non-hydrogen atoms were refined anisotropically. The H atoms attached to O atoms were located by differential Fourier analysis and refined with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{O})$. The positions of other H atoms were calculated geometrically and refined as riding, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$.

Crystallographic Data

Table S1. Experimental single crystal X-ray data for **1·iso-C₈**.

Formula	1·iso-C₈
Crystallization Solvent	isooctane/CHCl ₃ (= 1:1)
Collection Temperature (K)	173
Formula	C ₄₀ H ₄₅ Br ₄ O ₄ S ₄
Formula Weight	1037.64
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	23.9691(5)
<i>b</i> [Å]	31.1812(6)
<i>c</i> [Å]	19.7005(5)
α [°]	90.0000
β [°]	113.624(3)
γ [°]	90.0000
<i>V</i> [Å ³]	13489.9(6)
<i>Z</i>	12
<i>D</i> _{calcd} [g cm ⁻³]	1.533
<i>F</i> (000)	6252
2 θ _{max} [°]	26.000
Reflections collected / unique	26470 / 17431 [<i>R</i> _{int} = 0.0448]
Data / restraints / parameter	17431 / 534/ 1568
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>RI</i> = 0.0622, <i>wRI</i> = 0.1512
<i>R</i> indices (all data)	<i>RI</i> = 0.1031, <i>wRI</i> = 0.1780
Good-of-fit on <i>F</i> ²	1.027
Largest different peak and hole [e.Å ⁻³]	1.048 and -0.6282
CCDC	2063587

Vapor sorption measurement of the activated crystal **1a toward isooctane and *n*-heptane**

Pre-treatment: Before vapor adsorption measurement, the solvent-free **1a** has been pretreated at 100°C at $< 10^{-3}$ Torr for 1 days for **1** just prior to use by the installed equipment of a BELSORP 18 automated gas adsorption apparatus. The two alkanes were treated with CaH₂ to remove water as an impurity component, followed by distillation at N₂ atmosphere, were stored by using molecular sieves 3A.

Vapor adsorption measurement: Adsorption measurement of **1a** for the two alkane vapors were conducted by using the BELSORP 18 automated gas adsorption apparatus. The activated crystal **1a** was placed in the sample chamber (ca. 15 mL) maintained at $25.0 \pm 0.1^\circ\text{C}$. The larger gas chamber (176.36 mL) with a pressure gauge was kept at $50 \pm 0.1^\circ\text{C}$. Helium gas at certain pressure was introduced in the gas chamber and was allowed to diffuse into the sample chamber by opening a valve. The change in pressure allowed an accurate determination of volume of the total gas phase. Host-guest complexation was monitored in a similar manner by using a guest vapors in place of helium. The amount of guest adsorbed was calculated readily from the pressure difference ($P_{\text{cal}} - P$), where, P_{cal} is the calculated pressure if there were no guest adsorption, as in the case of helium, and P is the observed equilibrium pressure, as which the change in pressure in 500 sec had become smaller than 1 % of the pressure at the point. All operations were computer-controlled and automatic.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was recorded on a HITACHI STA7300 apparatus in the temperature range between 30 and 500 °C under a nitrogen atmosphere at a heating rate 10 °C min⁻¹.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was recorded on a HITACHI DSC7000X apparatus in the temperature range between 40 and 120 °C under a nitrogen atmosphere at a heating and cooling rates 10 °C min⁻¹.

Gas chromatography with head-space method

Gas chromatography analyses were carried out on a Shimazu GC-2010 Plus with a DB-624 column (0.53 mm ID×30 m, 0.3 µm) by head-space method (a PerkinElmer TurboMatrix HS 40). The following GC method was used as follow; the oven was programmed from 40°C, ramped at 10°C min⁻¹ increments to 240°C 10 min hold, the total run time was 60 min; injection temperature 140°C; detection temperature 250°C, and flow rate (line velocity) 35 cm sec⁻¹ with helium (carrier gas).

2. Supporting figures

Sorption Experiment in Vials

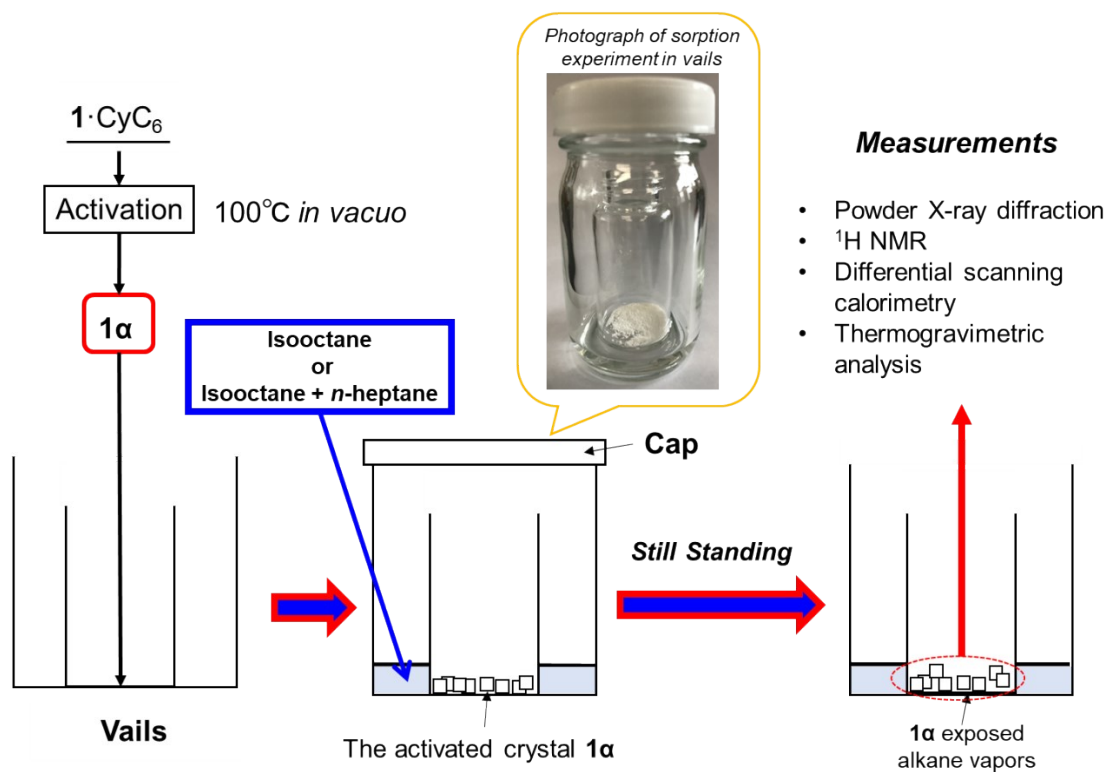


Figure S1 Sorption experiments of single or two-component alkane vapors by the activated crystal 1α for isooctane (*iso*- C_8) and *n*-heptane (*n*- C_7) in vials.

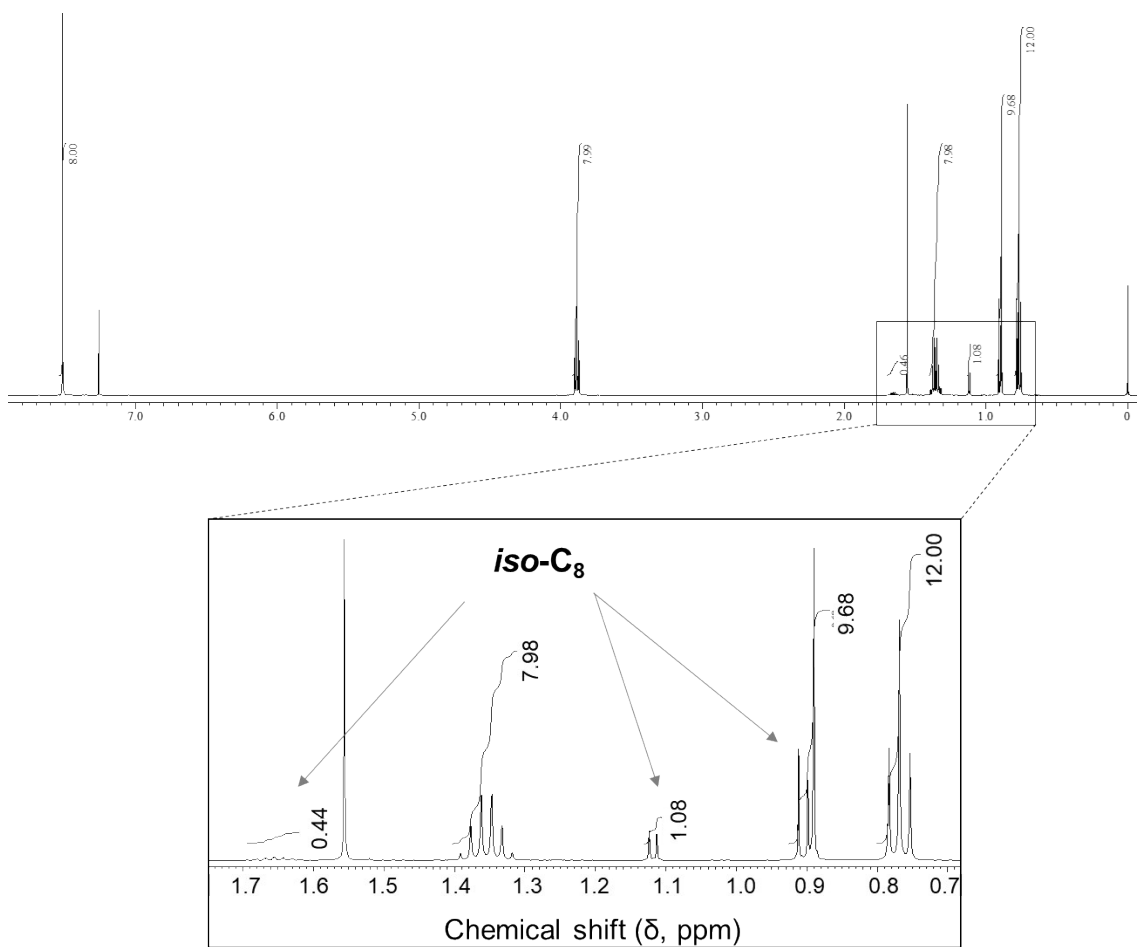


Figure S2 ^1H NMR spectrum after the activated crystal **1a** exposed to *iso-C₈* vapor.

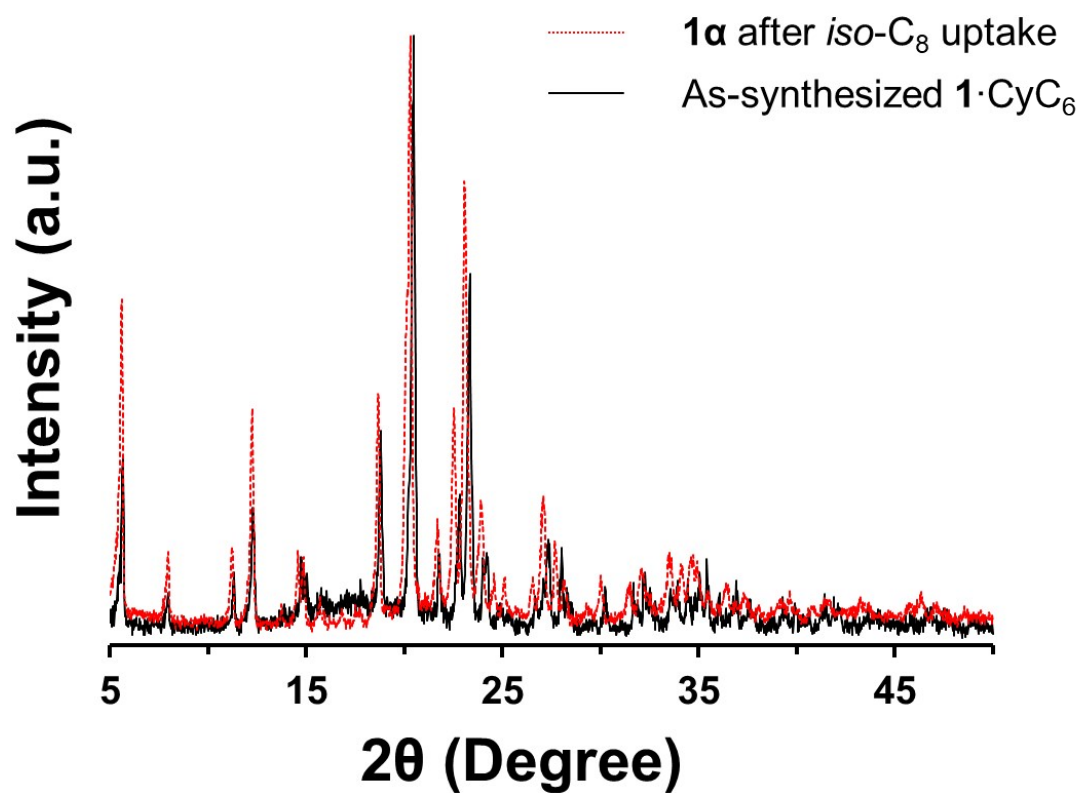


Figure S3 PXRD patterns of as-synthesized **1·CyC₆** (black, solid line) and the activated crystal **1α** exposed to *iso*-C₈ vapor in vials (red, dotted line).

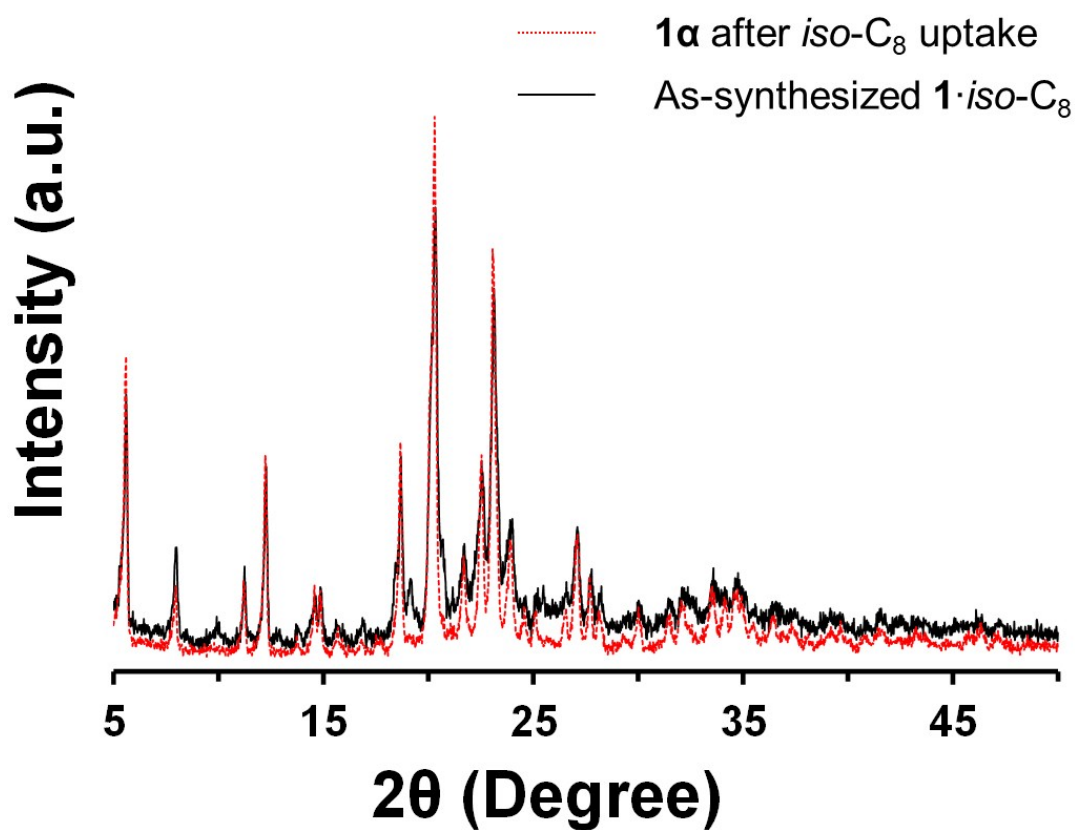


Figure S4 PXRD patterns of as-synthesized **1**·*iso*-C₈ (black, solid line) and the activated crystal **1α** exposed to *iso*-C₈ vapor in vials (red, dotted line).

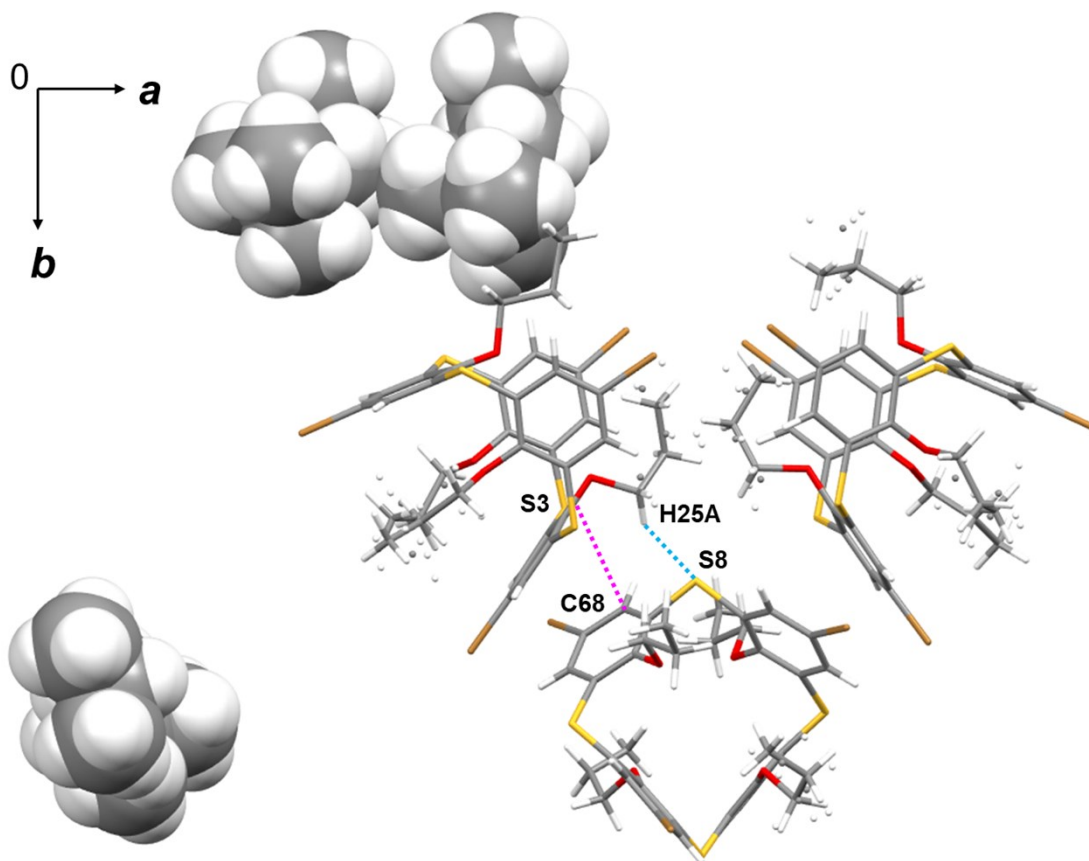


Figure S5 An asymmetrical unit of single crystal $1 \cdot iso-C_8$ was comprised by three thiacalixarene molecules (stick models) and three disordered isooctane molecules (space filling model). Propyl moieties as a partial of three thiacalixarenes were disordered and the disordered parts were shown by gray and white circles around propyl moieties. Color code: Br = brown, Cl = light green, S = yellow, O = red, C = dark gray, H = light gray.

Two intermolecular interactions were observed in the asymmetrical unit; S- π interaction and S-H hydrogen bonding.

These distances of S- π interaction^{S7} and S-H hydrogen bonding were 3.395(6) and 2.843 Å, respectively.

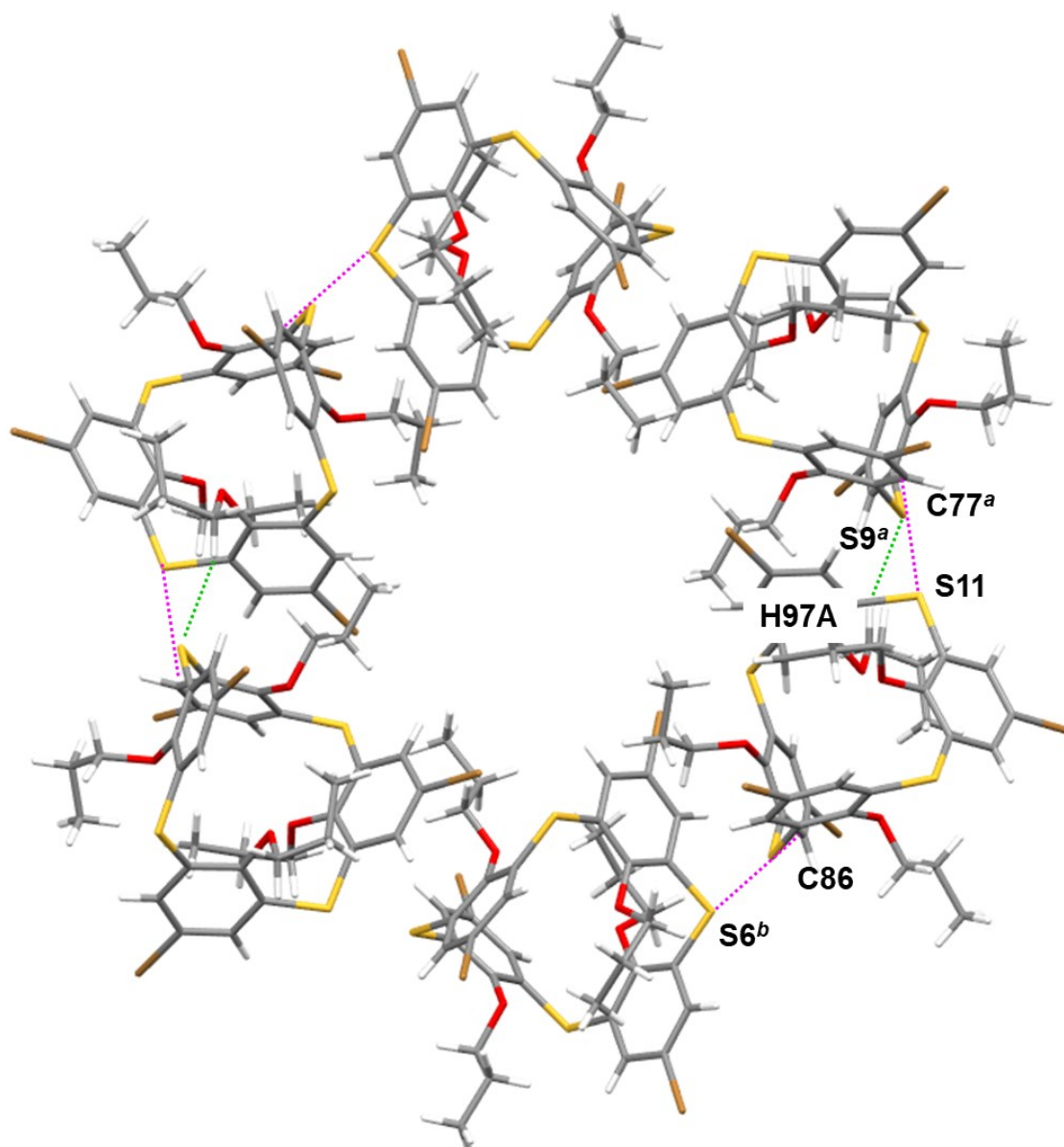


Figure S6 Projection of intermolecular S-H hydrogen bonding (green dotted lines) and S- π (purple dotted line) interactions supporting formation of a 1D preorganized channel-like void of **1**·*iso*-C₈ assembling by S- π interactions^{S7} and S-H hydrogen bonding. Color code: Br = brown, Cl = light green, S = yellow, O = red, C = dark gray, H = light gray.

Symmetry operations: ^a $x, 1/2-y, -1/2+z$; ^b $2-x, -1/2+y, 3/2-z$

Selected distances (Å): S11... C77^a 3.493(7), S9^a...H97A 2.786, and S6^b...C86 3.466(6) Å.

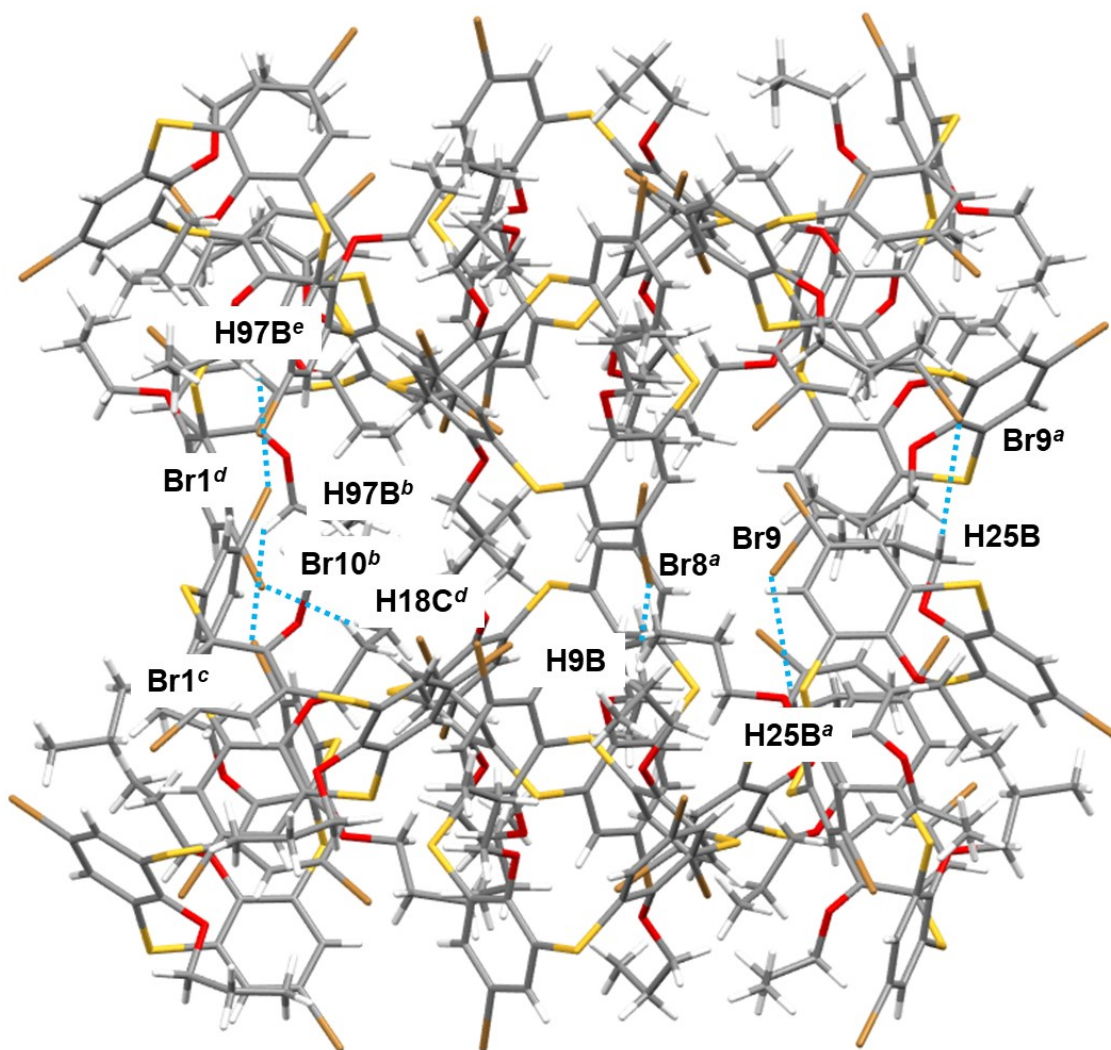


Figure S7 Projection of intermolecular Br-H (light blue dotted line) contacts supporting formation of pillar units in the 1D channel-like structure of **1**·*iso*-C₈. Color code: Br = brown, Cl = light green, S = yellow, O = red, C = dark gray, H = light gray.

Symmetry operations: ^a $x, 1/2-y, -1/2+z$; ^b $2-x, -1/2+y, 3/2-z$; ^c $1-x, -y, 1-z$; ^d $1-x, -1/2+y, 1/2-z$; ^e $2-x, -y, 1-z$

Selected distances (Å): Br9[⋯]H25B^a 2.996, Br8^a[⋯]H9B 3.047, Br1^c[⋯]H97B^b 2.9530, Br10^b[⋯]H18C^d 2.983.

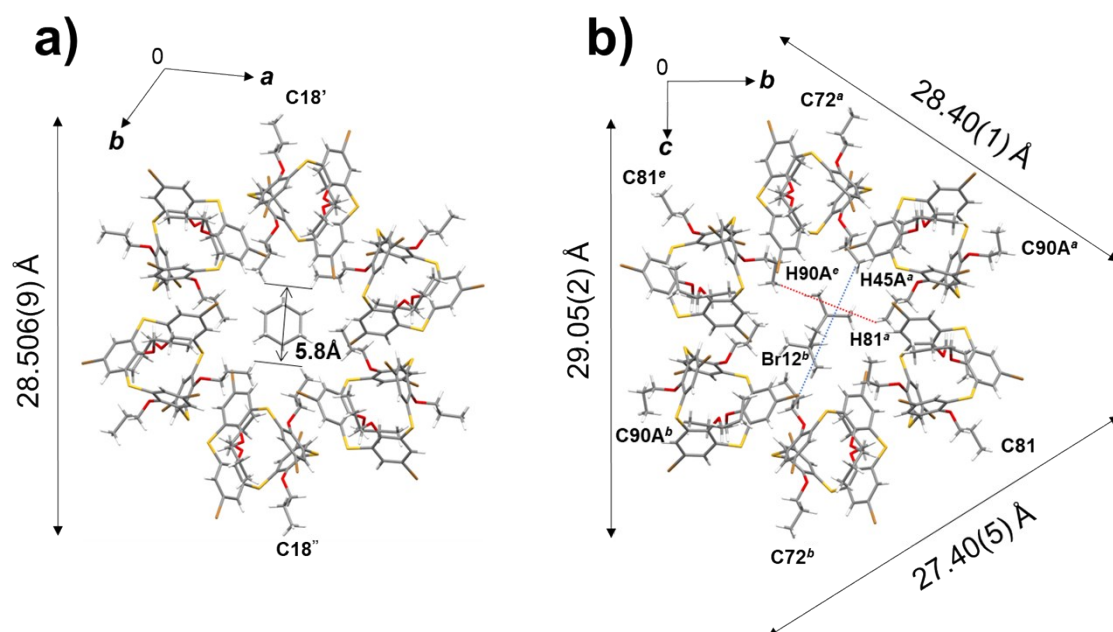


Figure S8 Projection of the void sizes and the assembly size of the two extended structures of a) $1 \cdot \text{CyC}_6$ and b) $1 \cdot \text{iso-C}_8$. Br = brown, Cl = light green, S = yellow, O = red, C = dark gray, H = light gray.

Symmetry operations: $^1 1-x, -x+y, 1/2-z$; $^2 1/3+x, 2/3+x-y, 1/6+z$; $^a x, 1/2-y, -1/2+z$; $^b 2-x, -1/2+y, 3/2-z$; $^e 2-x, -y, 1-z$

Selected distances (Å): $\text{C18}' \cdots \text{C18}''$ 28.506(9) Å, $\text{C72}^a \cdots \text{C72}^b$ 29.05(2), $\text{C81} \cdots \text{C81}^e$ 28.40(1), $\text{C90A}^a \cdots \text{C90A}^b$ 27.40(5), $\text{Br12}^b \cdots \text{H45A}^a$ 9.7747, $\text{H90A}^e \cdots \text{H81}^a$ 7.3459.

How to measure the void sizes of $1 \cdot \text{CyC}_6$ and $1 \cdot \text{iso-C}_8$

A temporary atom was placed in the center between base H16 atom and neighboring H16 atom. Similarly, another temporary atom was placed in the symmetry of the temporary atom described above. The void size of $1 \cdot \text{CyC}_6$ was obtained by measuring the distance between the temporary atoms, ca. 5.8 Å. The void size of $1 \cdot \text{iso-C}_8$ was measured by $\text{Br12}^b \cdots \text{H45A}^a$ and $\text{H90A}^e \cdots \text{H81}^a$ distances, ca. 9.8×7.3 Å.

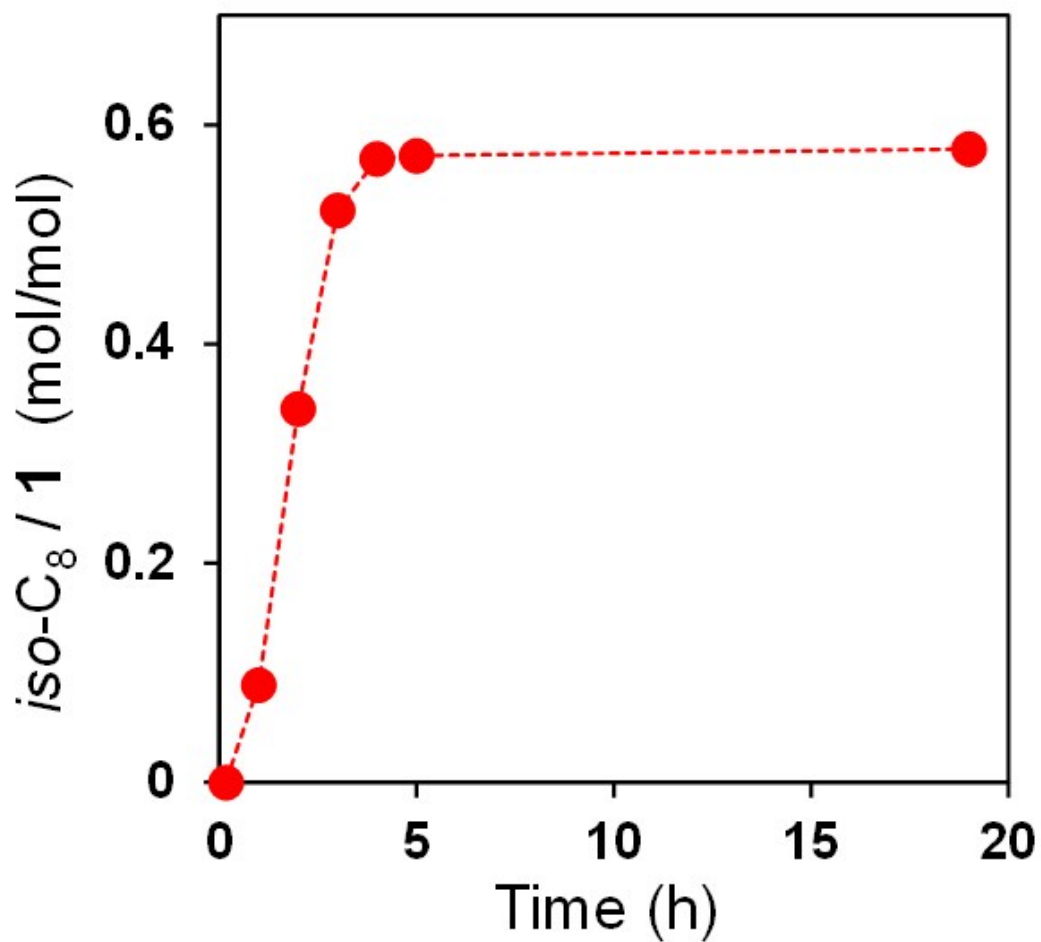


Figure S9 Time-dependent quantity adsorbed of *iso*-C₈ vapor by **1α**.

The number of adsorbed molecules is the adsorbed *iso*-C₈ / **1** ratio at the equilibrium state. The number was calculated by integrated intensities of adsorbed isooctane's chemical shifts when **1** was defined as one molecule from integrated ¹H NMR intensities.

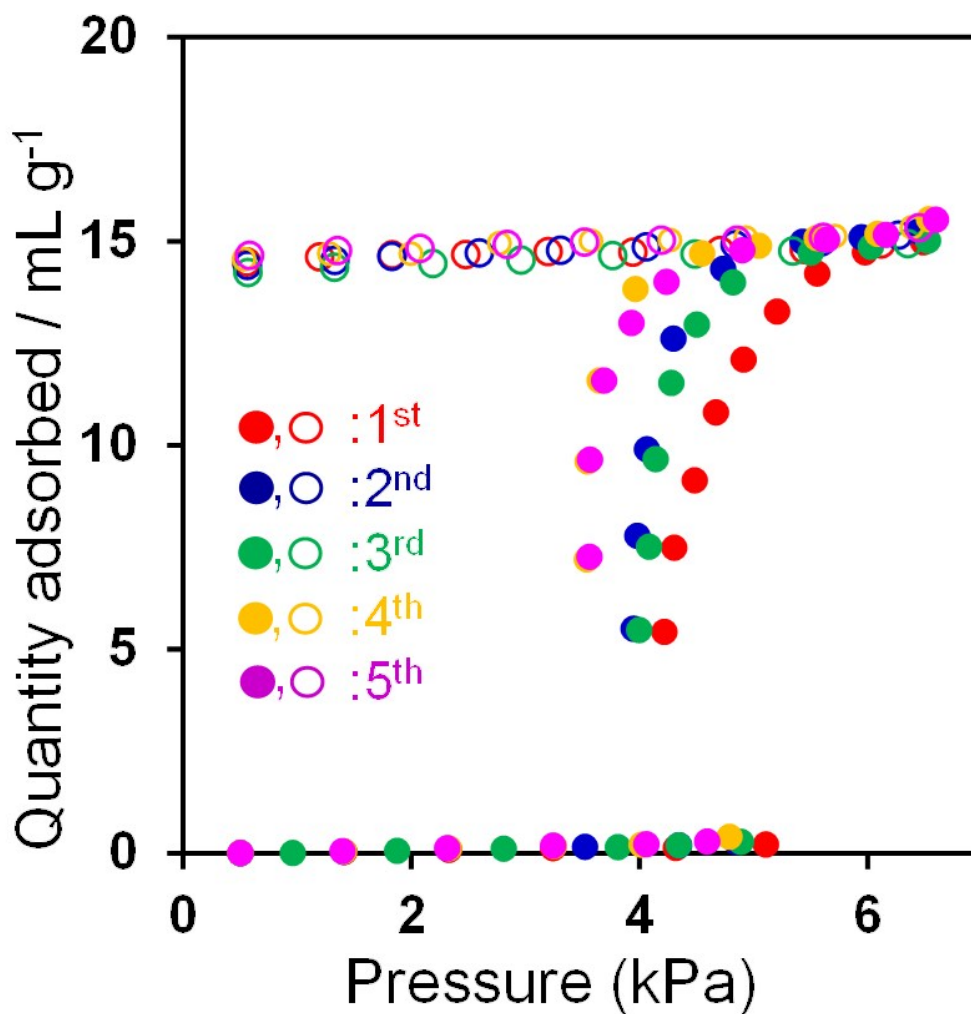


Figure S10 Sorption isotherms of *iso*-C₈ vapor at 25 °C of the activated crystal **1a** at the 1st cycle (red circles) and the re-activated crystal **1a** at the 2nd – 5th cycles (blue, green, yellow, and pink circles). Solid symbols: sorption; open symbols: desorption.

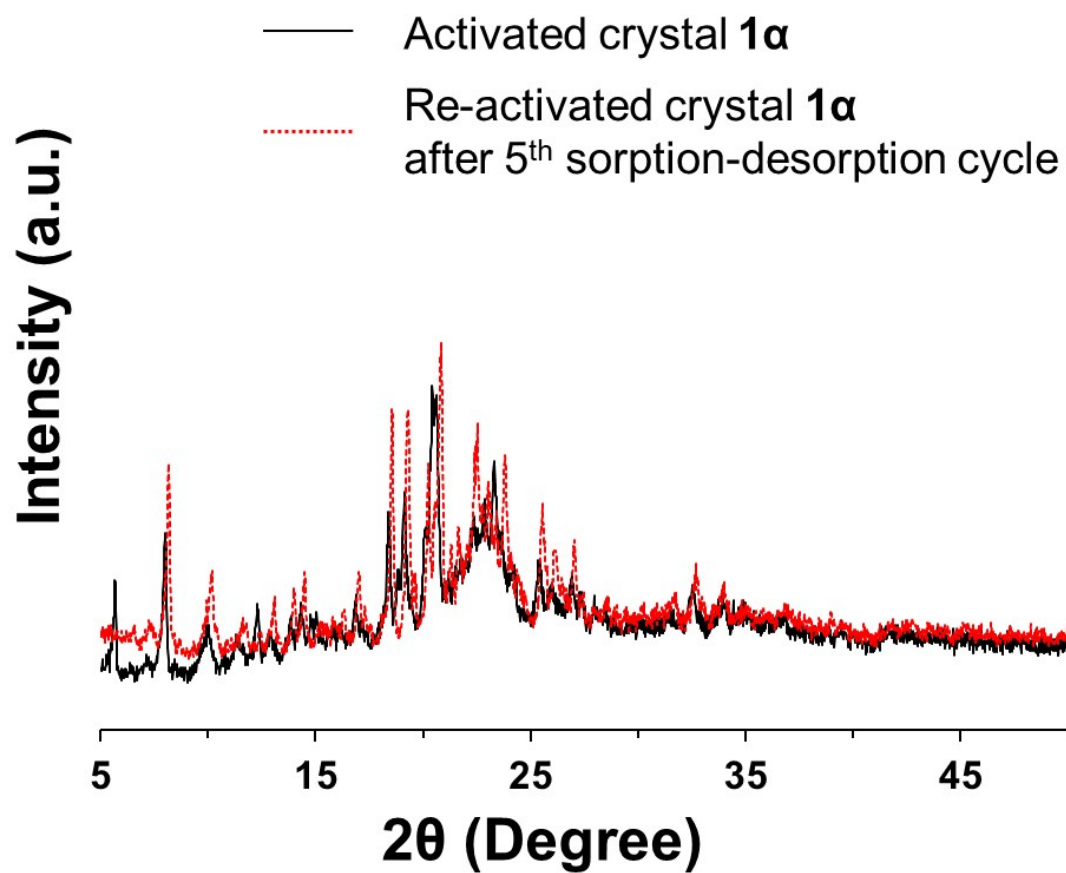


Figure S11 PXR D patterns of the activated crystal 1α (black, solid line) and the re-activated crystal 1α after 5th sorption-desorption cycle (red, dotted line).

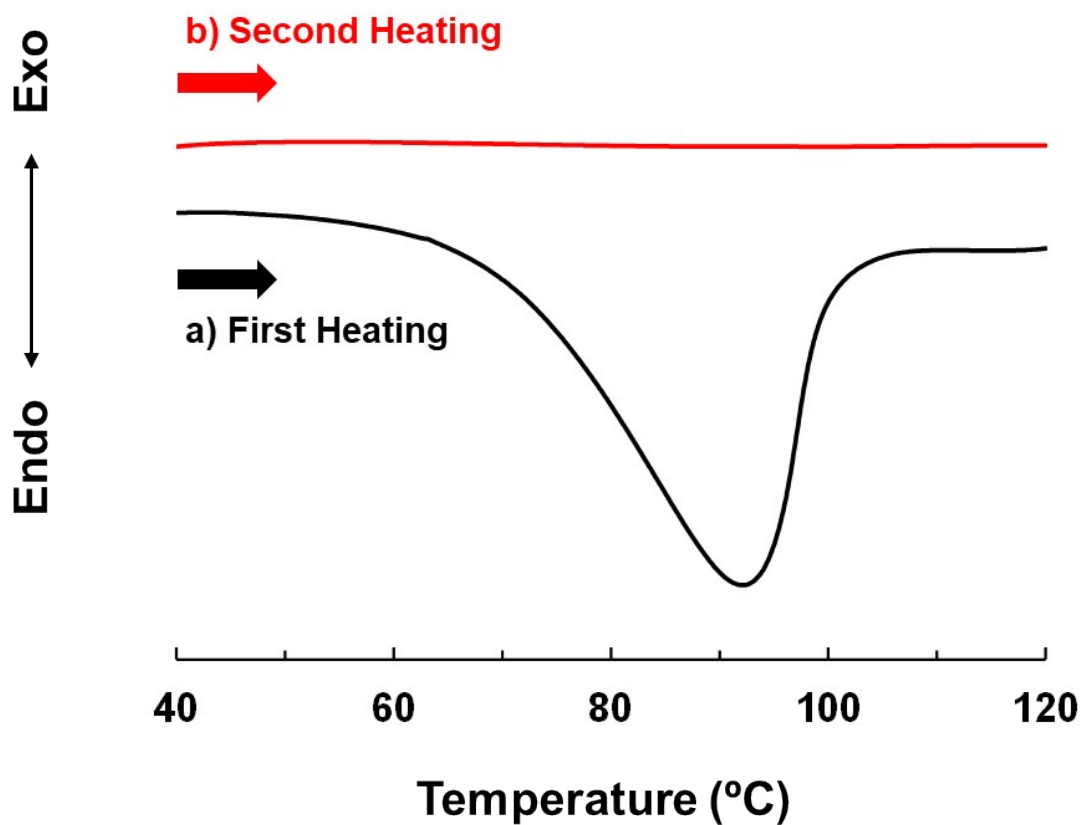


Figure S12 Heating curves of differential scanning calorimetry (DSC) of the **1a** adsorbed *iso*-C₈. a) In the first heating, endothermic peak was observed at 50-105 °C and b) no endothermic peak was not observed in the second heating.

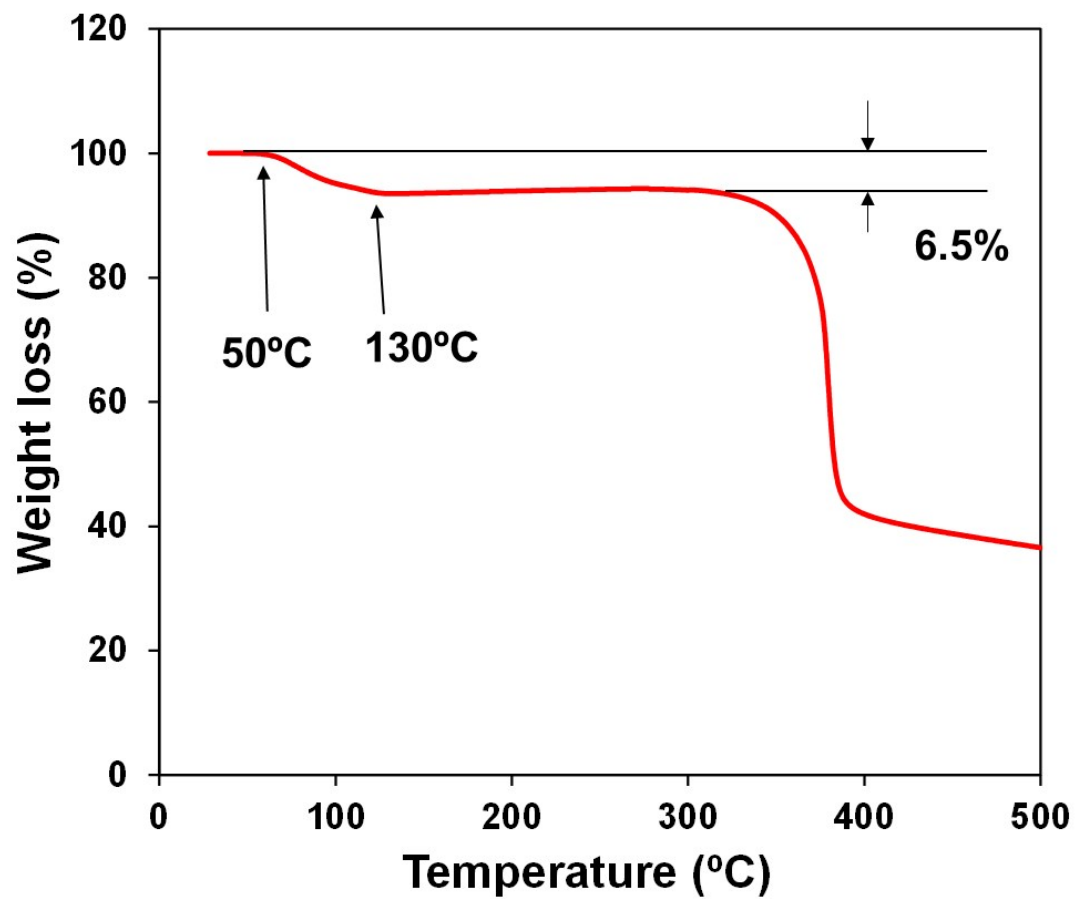


Figure S13 Thermogravimetric analysis (TGA) of the **1 α** adsorbed *iso*-C₈.

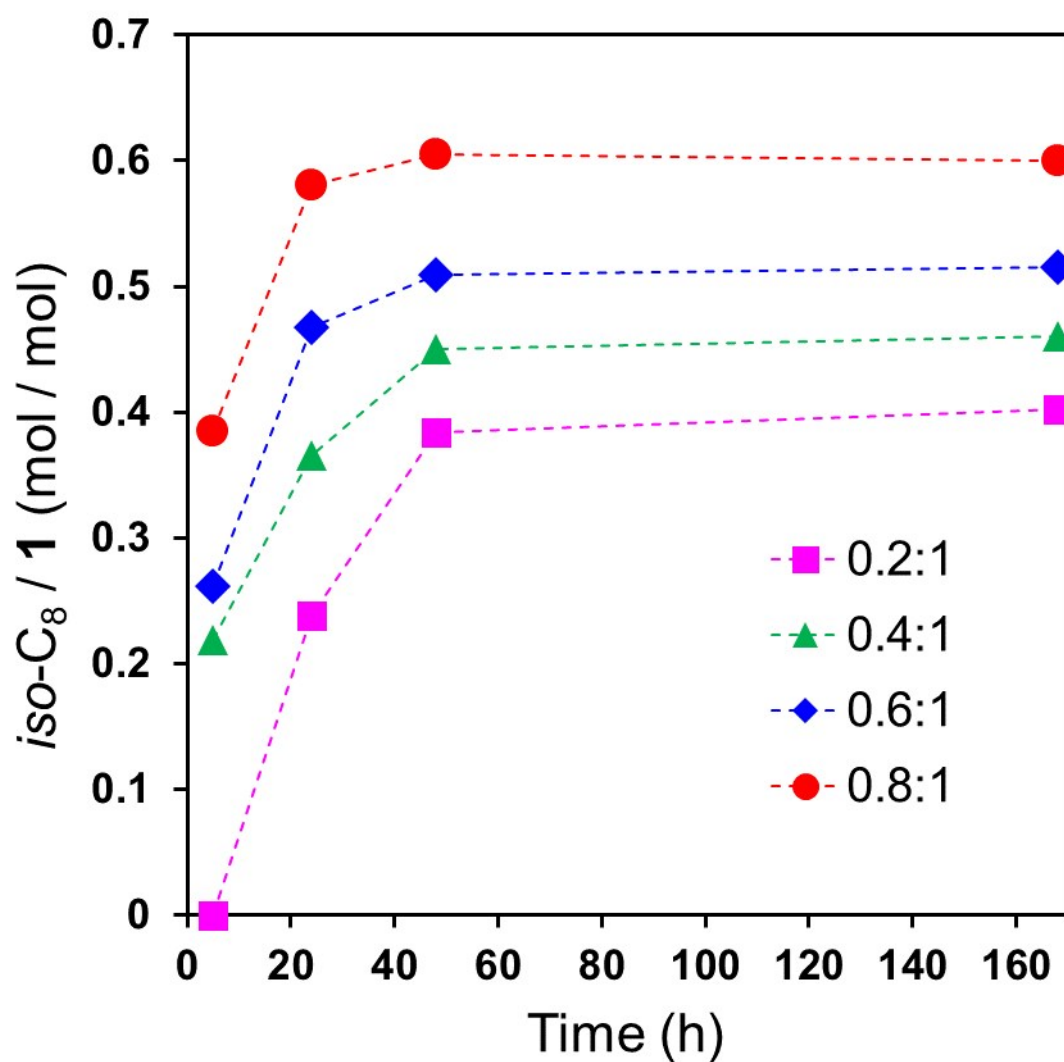


Figure S14 Change in quantity adsorbed of *iso*-C₈ over time when **1a** is exposed to *iso*-C₈/*n*-C₇ mixed system with different composition (*iso*-C₈:*n*-C₇ = 0.2:1–0.8:1).

The number of adsorbed molecules is the adsorbed *iso*-C₈ / **1** ratio at the equilibrium state. The number was calculated by integrated intensities of adsorbed isooctane's chemical shifts when **1** was defined as one molecule from integrated ¹H NMR intensities.

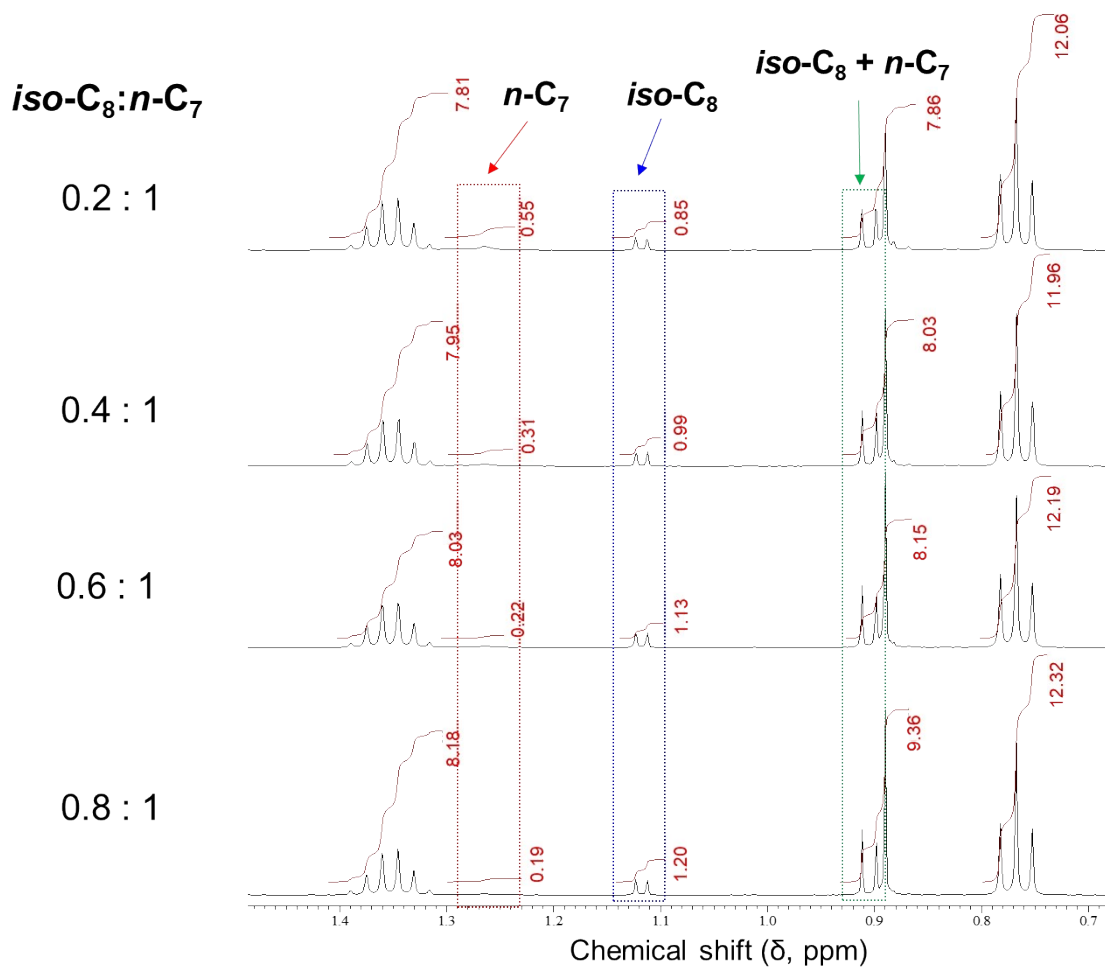


Figure S15 ¹H NMR spectra after **1a** exposed *iso*-C₈/*n*-C₇ mixed system at various compositions of *iso*-C₈ : *n*-C₇ = 0.2:1, 0.4:1, 0.6:1, and 0.8:1 for 48 h.

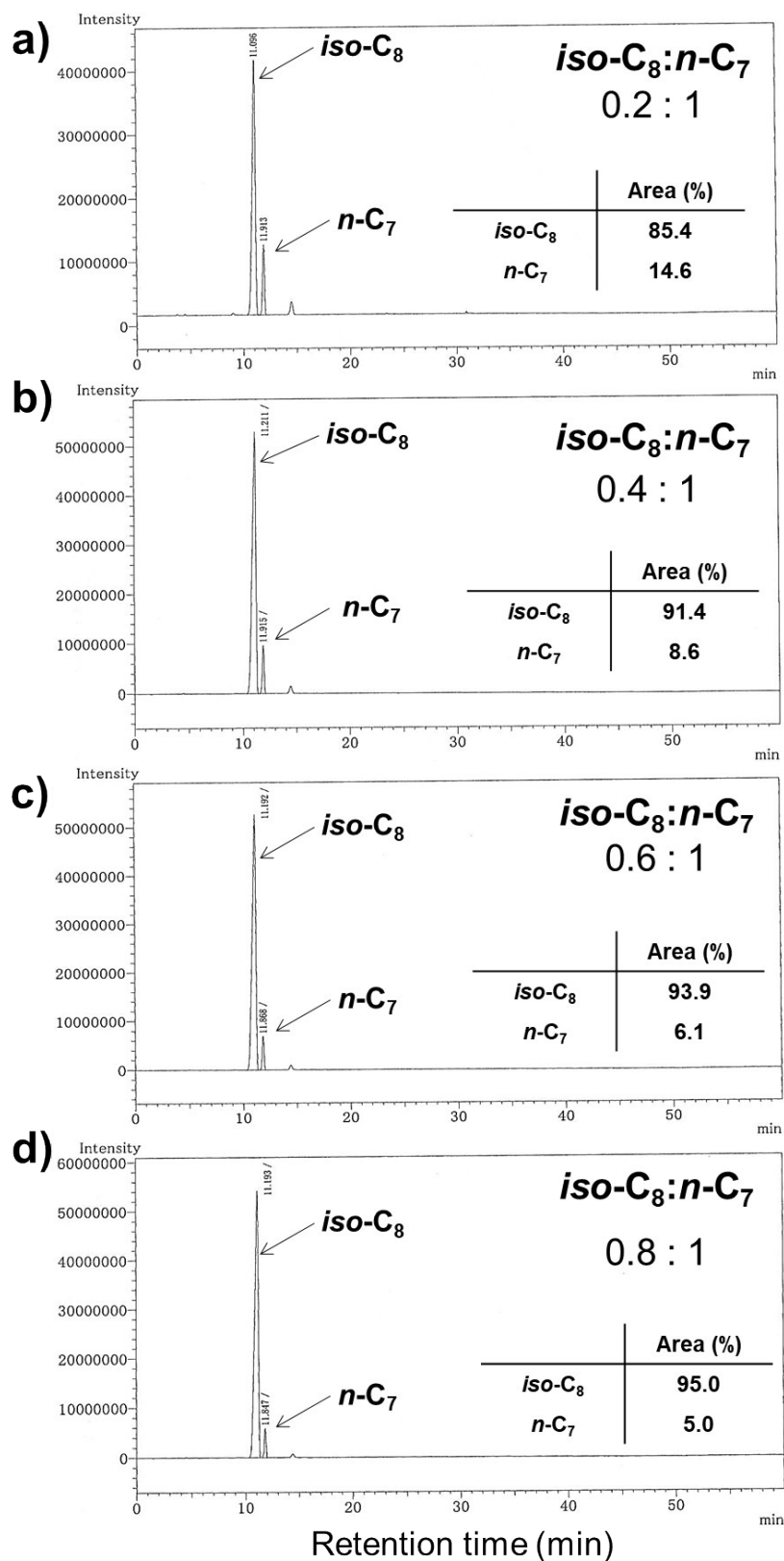


Figure S16 Gas chromatograms by head-space method for $iso-C_8/n-C_7$ ratio in **1a** which exposed $iso-C_8/n-C_7$ mixed system at various compositions of $iso-C_8 : n-C_7 =$ a) 0.2:1, b) 0.4:1, c) 0.6:1, and d) 0.8:1 for 48 h.

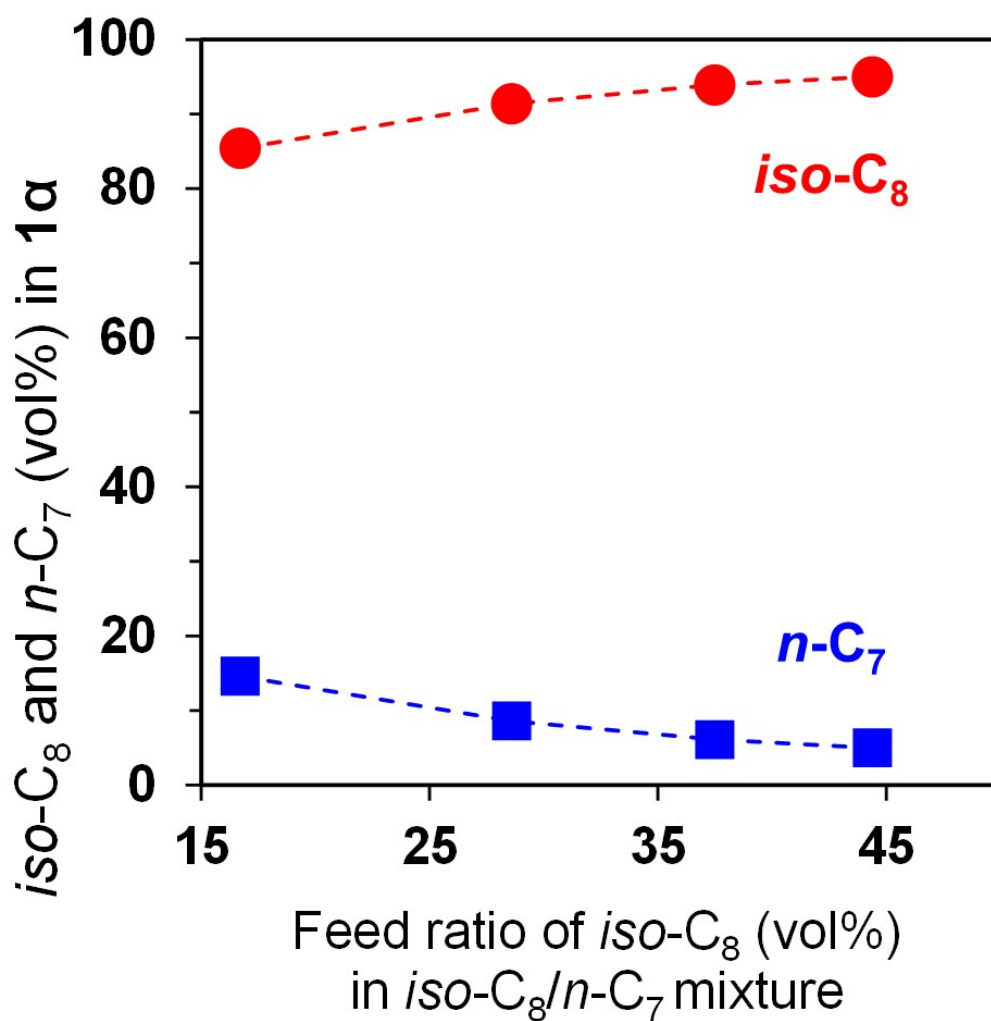


Figure S17 Gas-chromatographic analysis of RON upon the exposure of *iso-C*₈/*n-C*₇ mixed vapors (*iso-C*₈:*n-C*₇ ratio = 0.2:1–0.8:1) to activated crystal **1α**.

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