

Supporting Information

**Crystalline thiacalixarene assembly for adsorption ability
toward linear and branched C6 alkane vapor isomers**

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3. References

1. Experimental Section

Materials

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

S2

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 K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA) with a graphite monochromator at a step width of $0.02^\circ 2\theta$ and a scan speed $2.000^\circ \text{ min}^{-1}$.

Vapor sorption experiments of the activated crystal **1a** toward five C6 alkanes

Pre-treatment: Before vapor adsorption experiments, the activated crystal **1a** was pretreated at 100°C under reduced pressure overnight for **1** just before using the vapor adsorption experiments. The activated crystal **1a** was confirmed by a ¹H NMR study to not remain cyclohexane (CyC6) in **1a**.

Vapor adsorption experiments: Adsorption experiments of **1a** for the five C6 alkane

vapors were conducted using two vials as shown in Figure S1. The activated crystal **1a** (0.2 g) placed in a small vial (5 mL) was inserted into a larger vial (30 mL), which was loaded with each C6 alkane (5 mL) or two-component alkane (the ratio = 1:1 (= 2.5 mL + 2.5 mL)), at ambient temperature and varying exposure times

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was recorded on a HITACHI STA7300 apparatus in the temperature range between 25 and 500 °C under a N₂ atmosphere at a heating rate of 10 °C min⁻¹.

Sorption Experiment in Vials

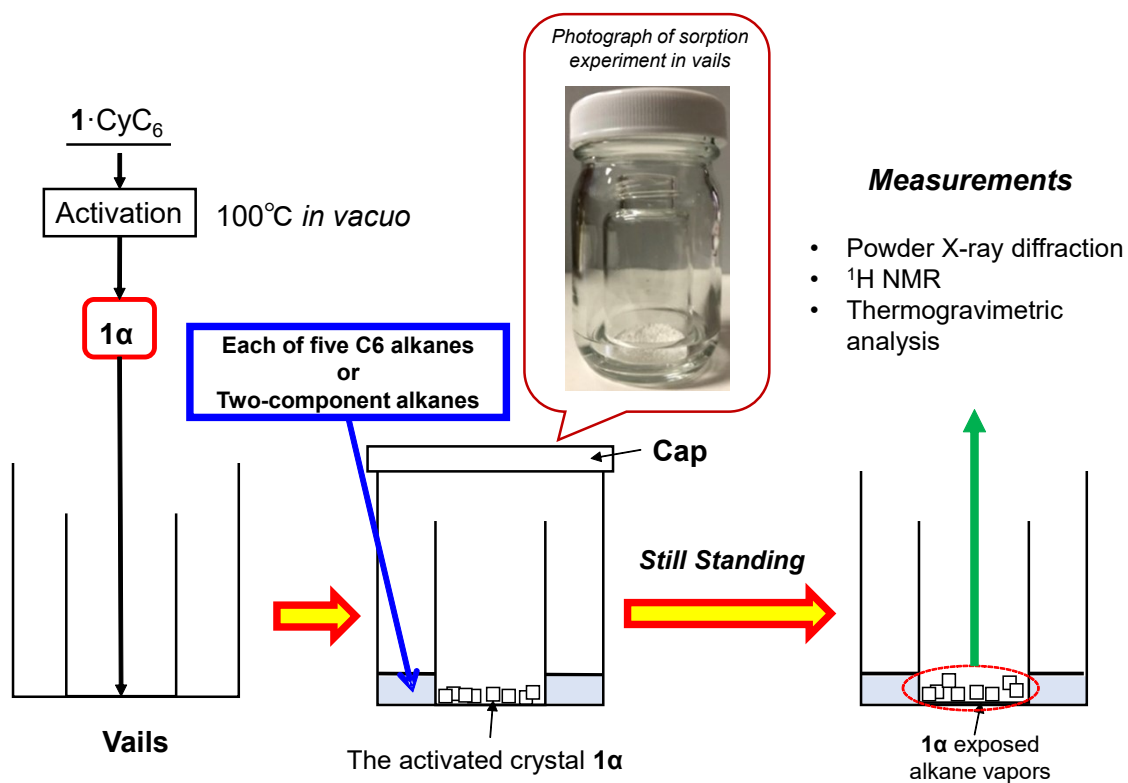


Figure S1 Sorption experiments of single or two-component alkane vapors by the activated crystal 1α for five C6 alkanes, such as *n*-hexane (*n*-C6), isohexane (2-C6), 3-methylpentane (3-C6), and 2,2- and 2,3-dimethylbutanes (2,2-C6 and 2,3-C6) in vials.

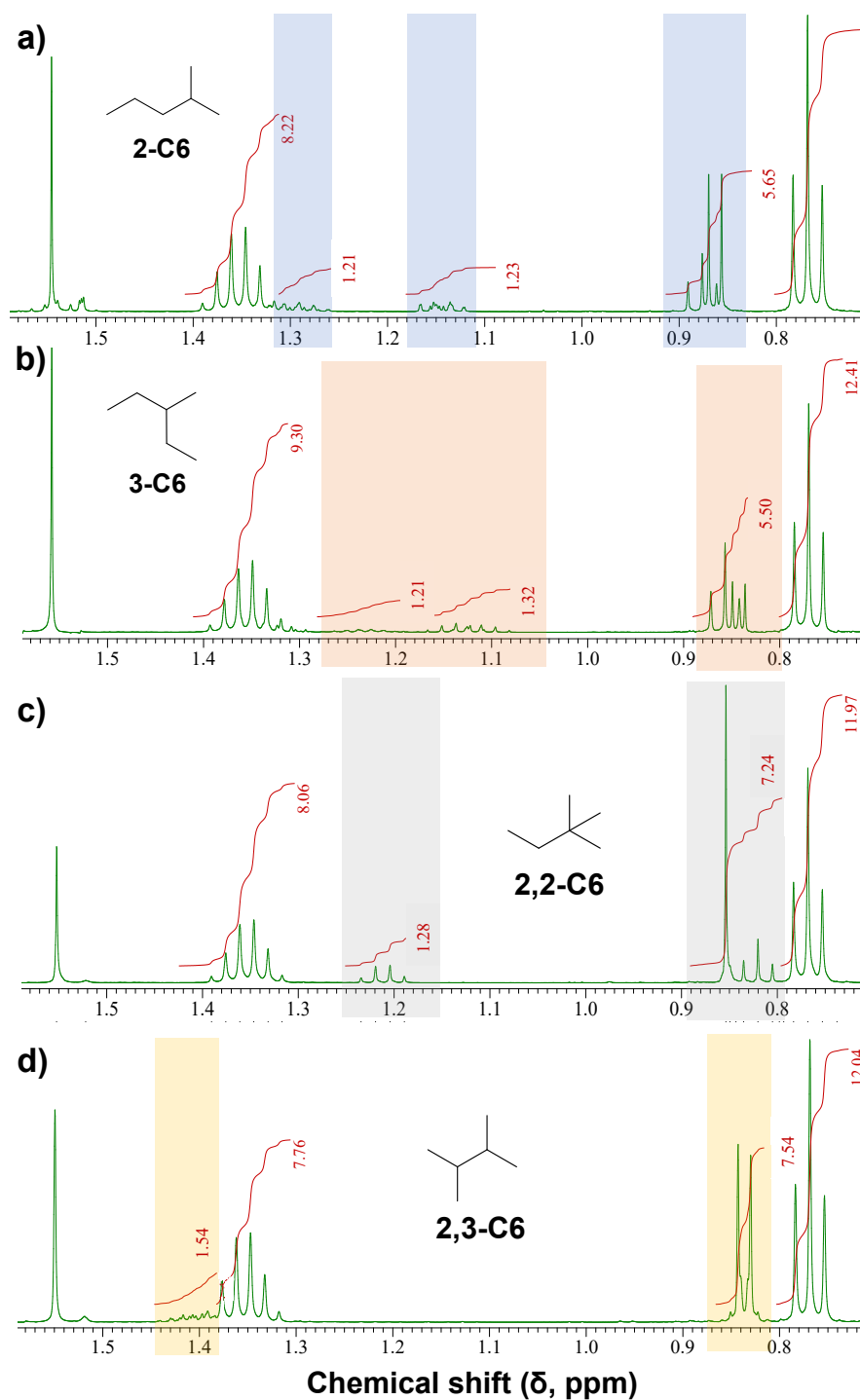


Fig. S2 500 MHz ^1H NMR spectra (δ from TMS, CDCl_3) after exposure of **1a** with C6 alkane vapors as each single component system. a) **1a** exposed to 2-C6, b) **1a** exposed to 3-C6, c) **1a** exposed to 2,2-C6, and d) **1a** exposed to 2,3-C6. The colored areas on the spectra indicate the regions where the respective chemical shifts of the C6 alkanes appear. The color codes: pale purple = *n*-C6; pale blue = 2-C6; pale orange = 3-C6; pale gray = 2,2-C6; pale yellow = 2,3-C6.

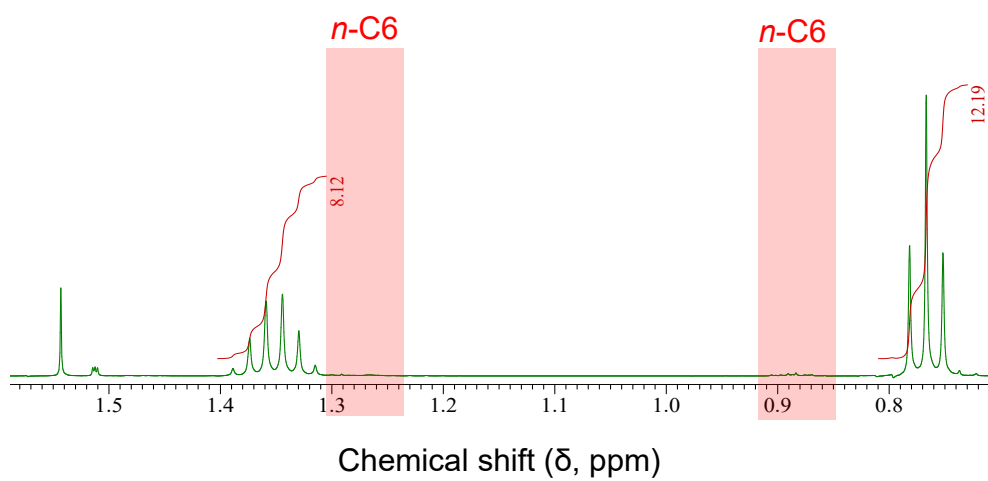


Fig. S3 500 MHz ¹H NMR spectra (δ from TMS, CDCl₃) after exposure of **1a** with *n*-C₆ alkane vapors as the single-component system. The color code: pink = *n*-C₆.

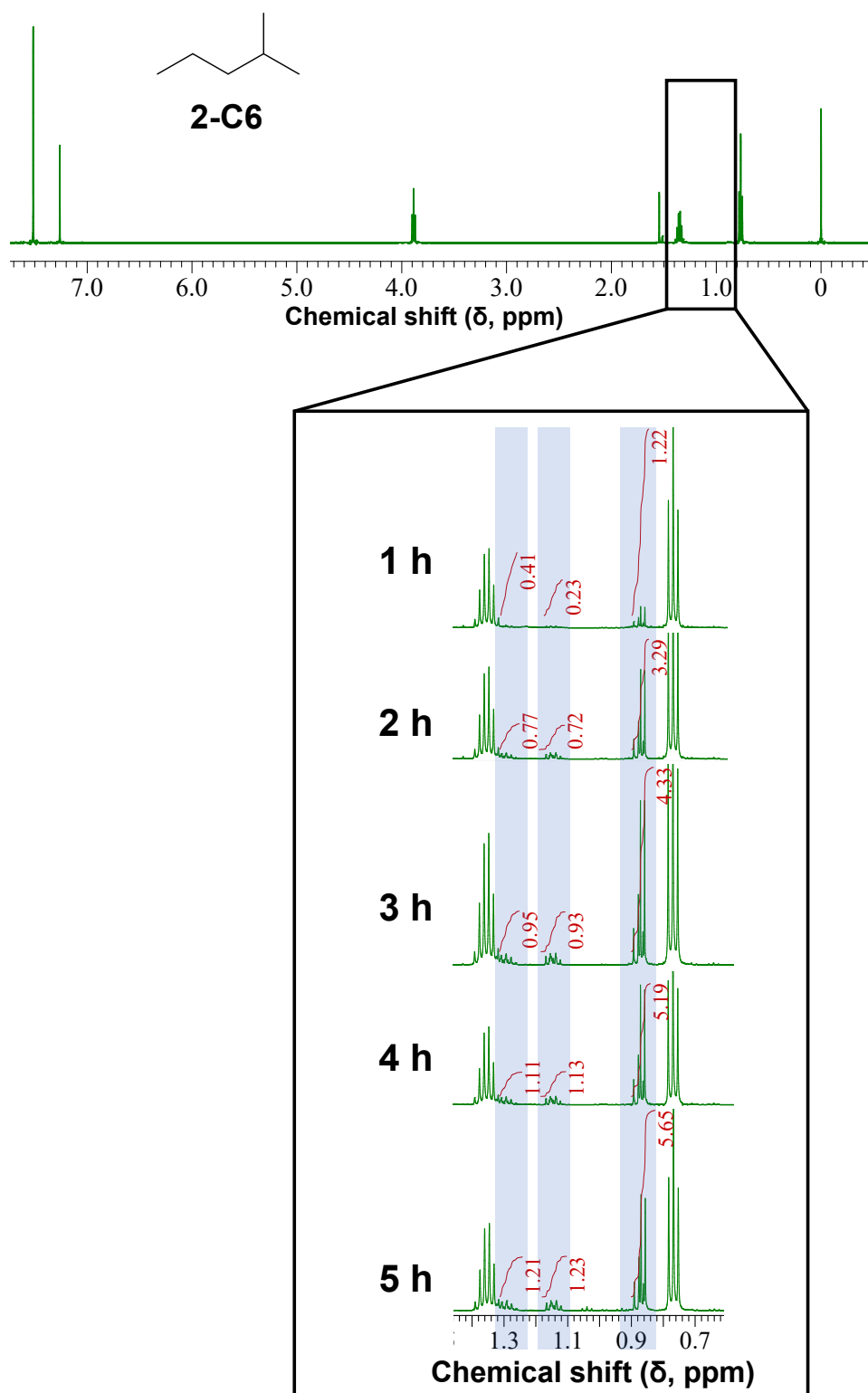


Fig. S4 500 MHz ¹H NMR spectrum (δ from TMS, CDCl₃) after exposure of **1a** with 2-C6 alkane vapors as a function of exposure time.

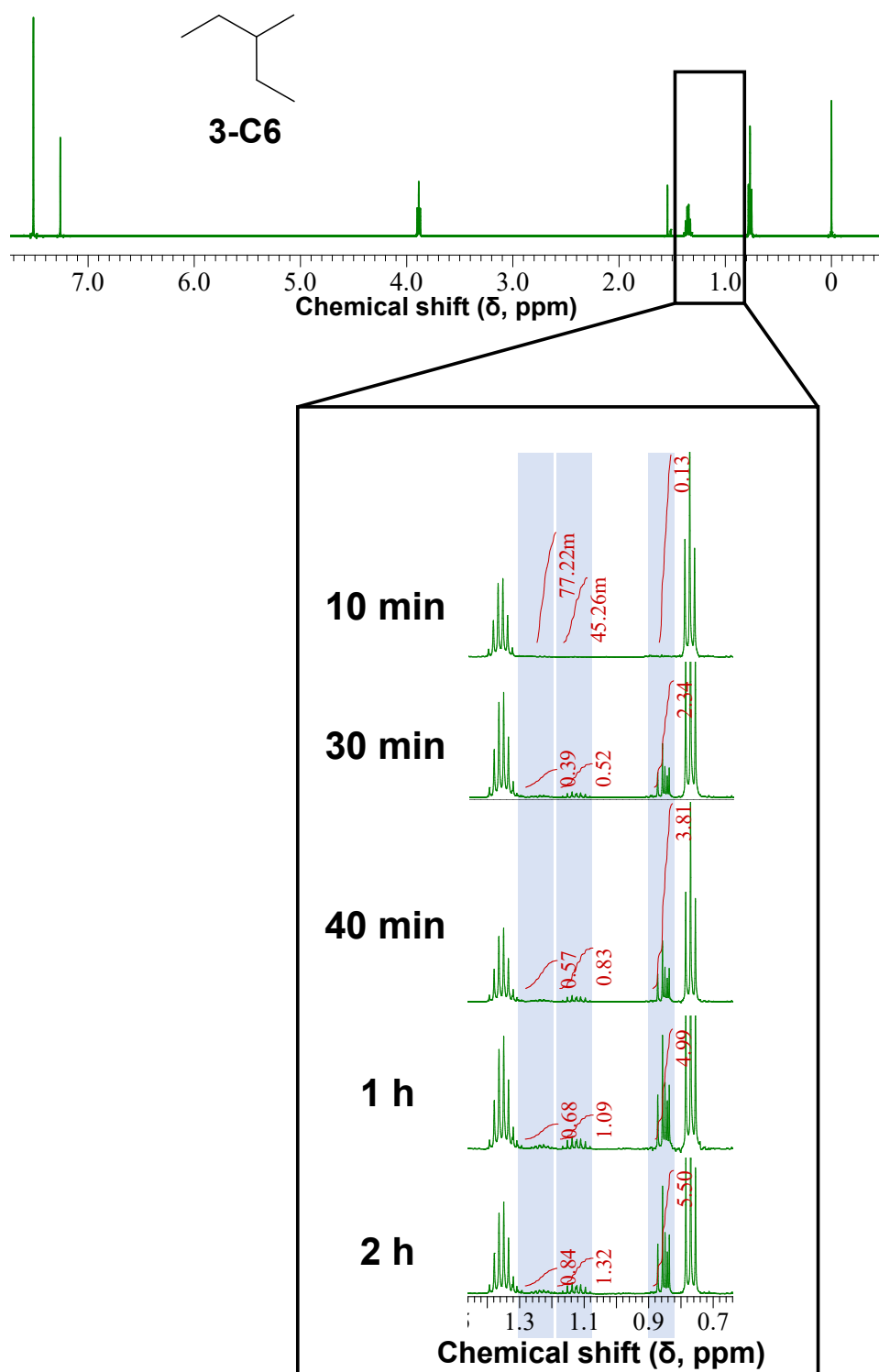


Fig. S5 500 MHz ¹H NMR spectrum (δ from TMS, CDCl₃) after exposure of **1a** with 3-C6 alkane vapors as a function of exposure time.

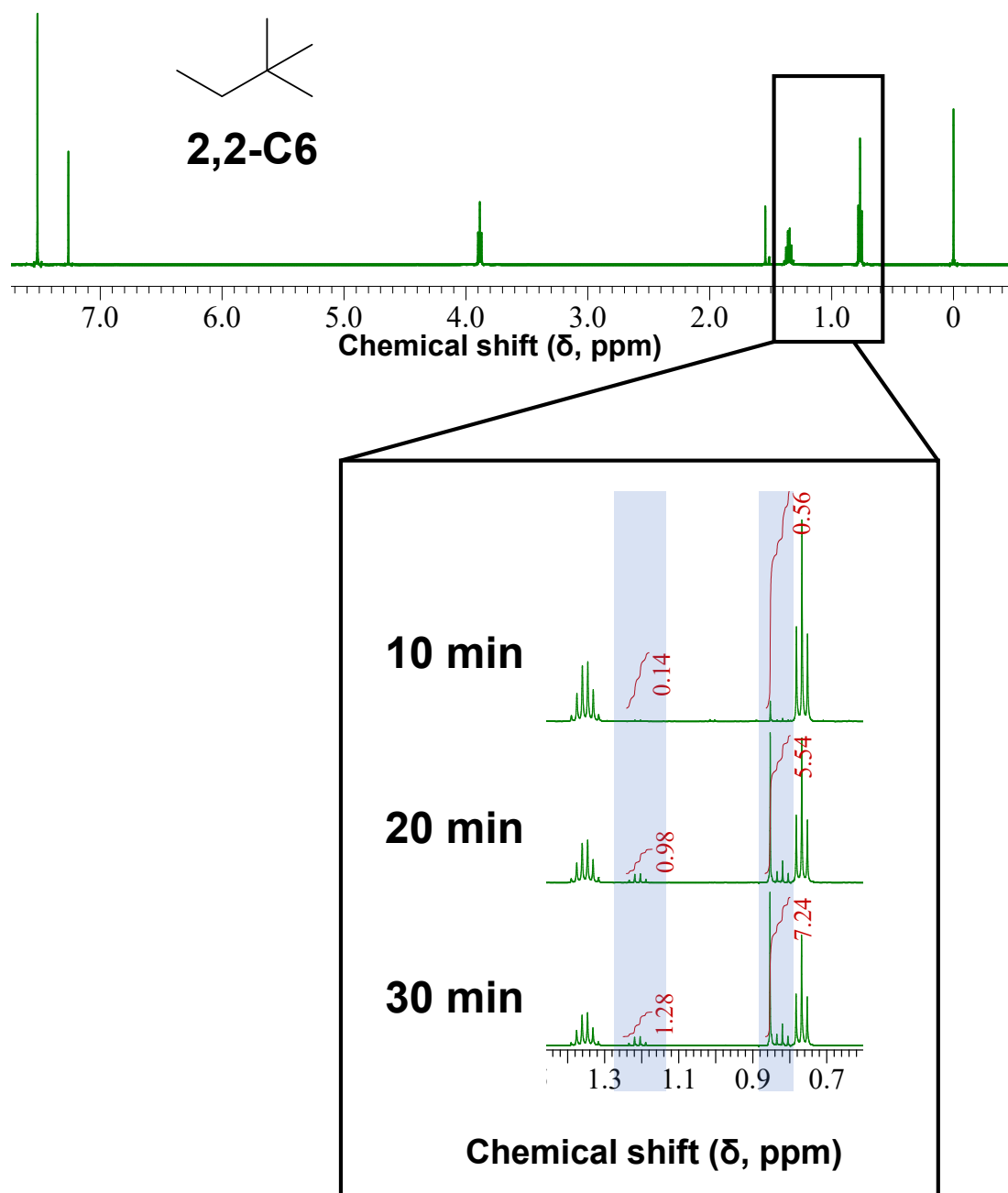


Fig. S6 500 MHz ¹H NMR spectrum (δ from TMS, CDCl₃) after exposure of **1a** with 2,2-C₆ alkane vapors as a function of exposure time.

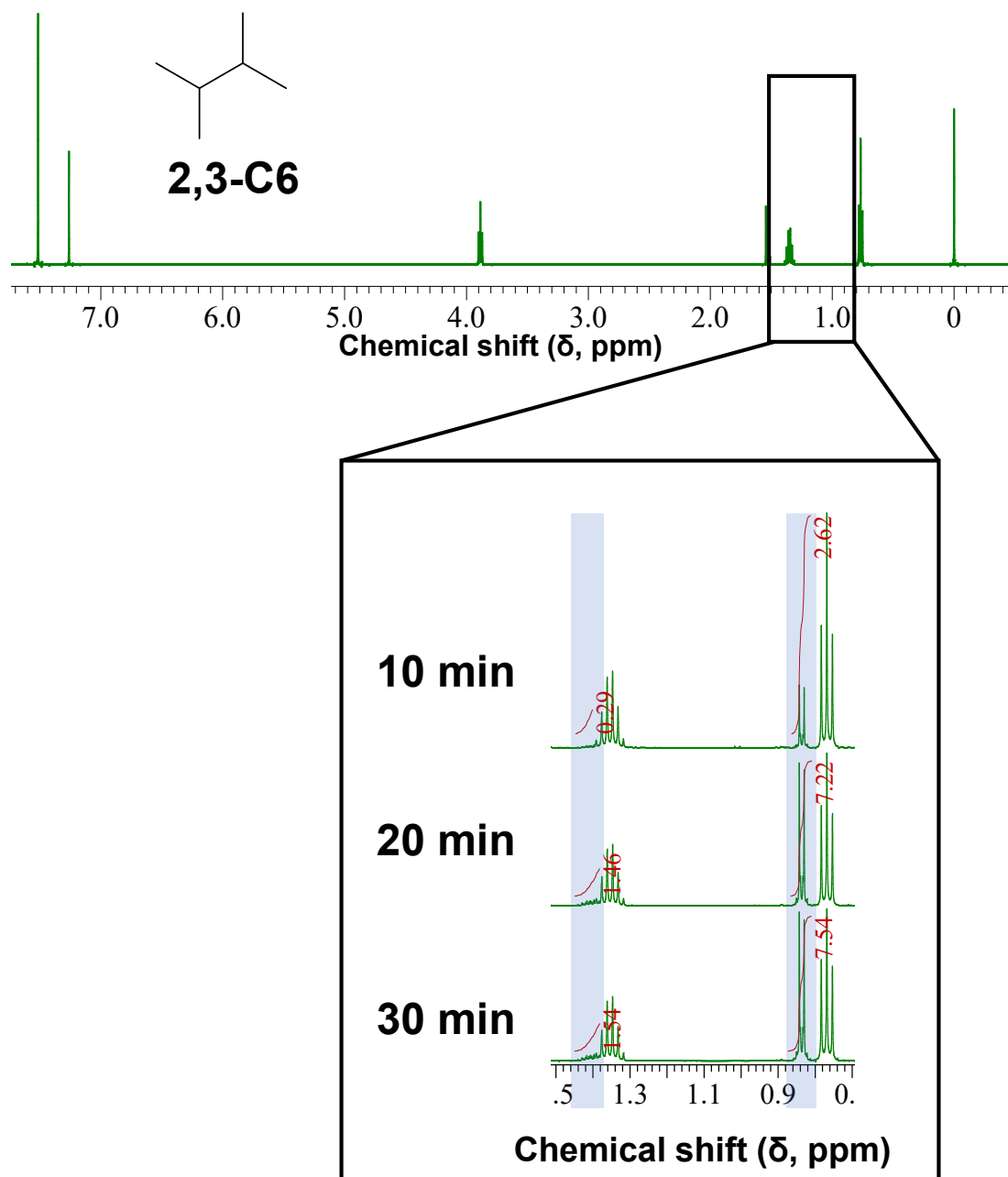


Fig. S7 500 MHz ¹H NMR spectrum (δ from TMS, CDCl_3) after exposure of **1a** with 2,3-C6 alkane vapors as a function of exposure time.

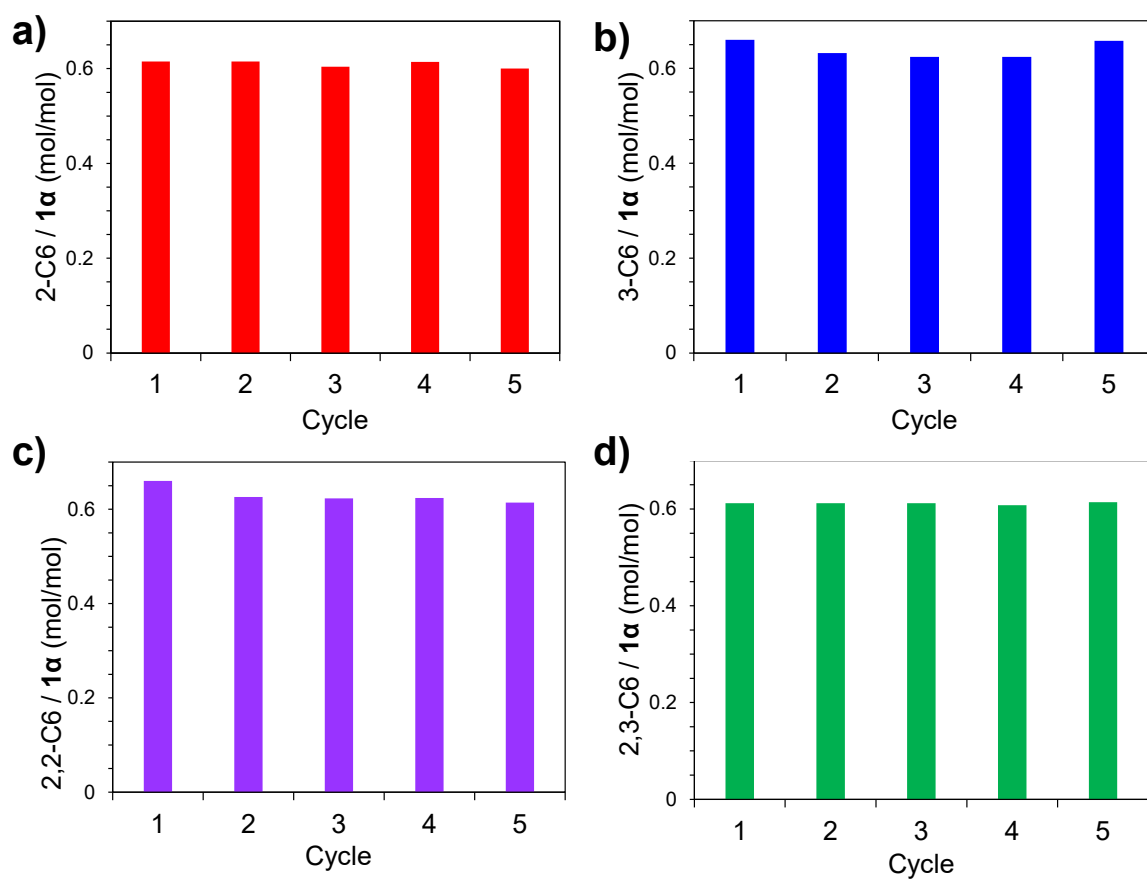


Fig. S8 Reusability and adsorbed quantities of 1α for adsorption of a) 2-, b) 3-, c) 2,2-, and d) 2,3-C6 vapors in 5th cycles.

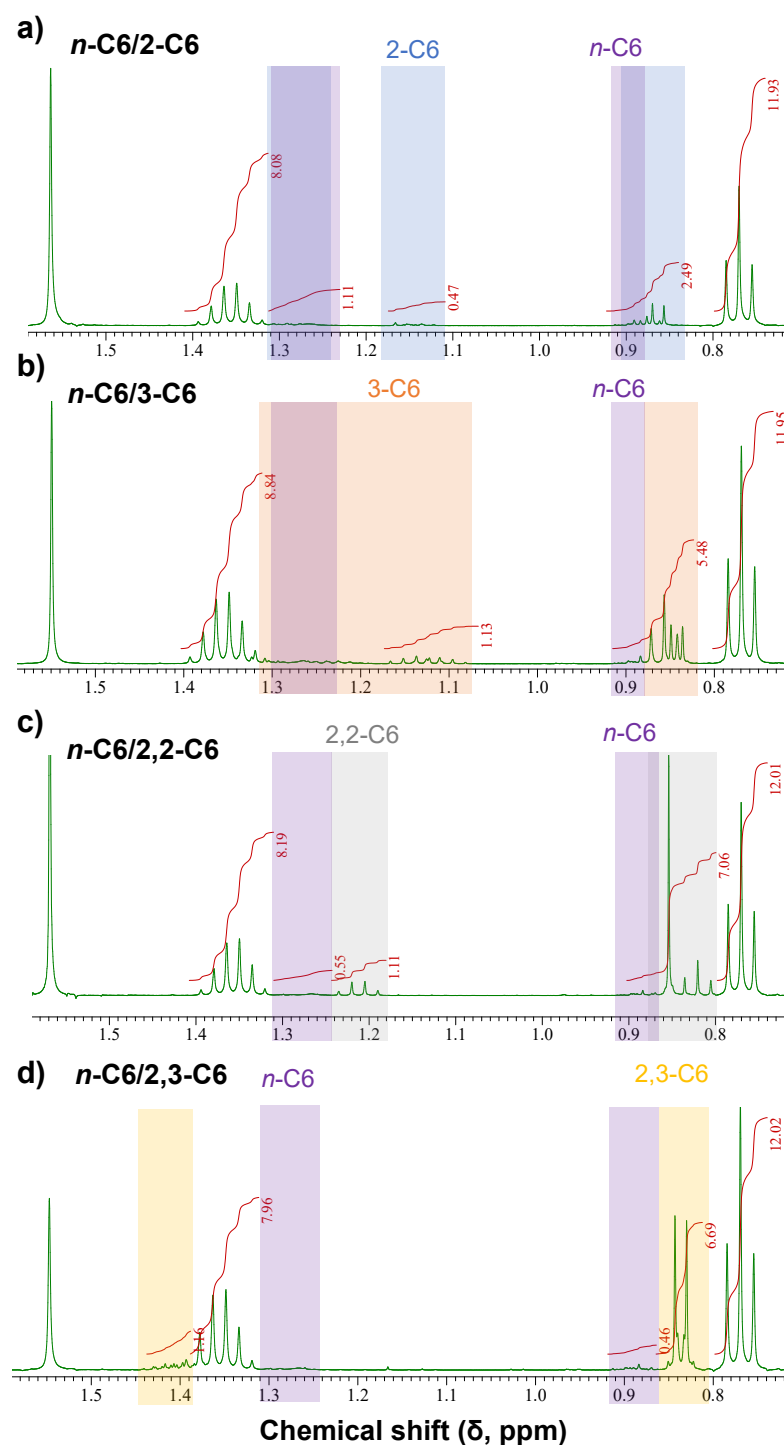


Fig. S9 500 MHz ^1H NMR spectra (δ from TMS, CDCl_3) after exposure of **1a** with $n\text{-C6}$ and branched alkane mixed vapors as each two-component system. a) **1a** exposed to $n\text{-C6}/2\text{-C6}$, b) **1a** exposed to $n\text{-C6}/3\text{-C6}$, c) **1a** exposed to $n\text{-C6}/2,2\text{-C6}$, d) **1a** exposed to $n\text{-C6}/2,3\text{-C6}$. The colored areas on the spectra indicate the regions where the respective chemical shifts of the C6 alkanes appear. The color codes: pale purple = $n\text{-C6}$; pale blue = 2-C6 ; pale orange = 3-C6 ; pale gray = $2,2\text{-C6}$; pale yellow = $2,3\text{-C6}$.

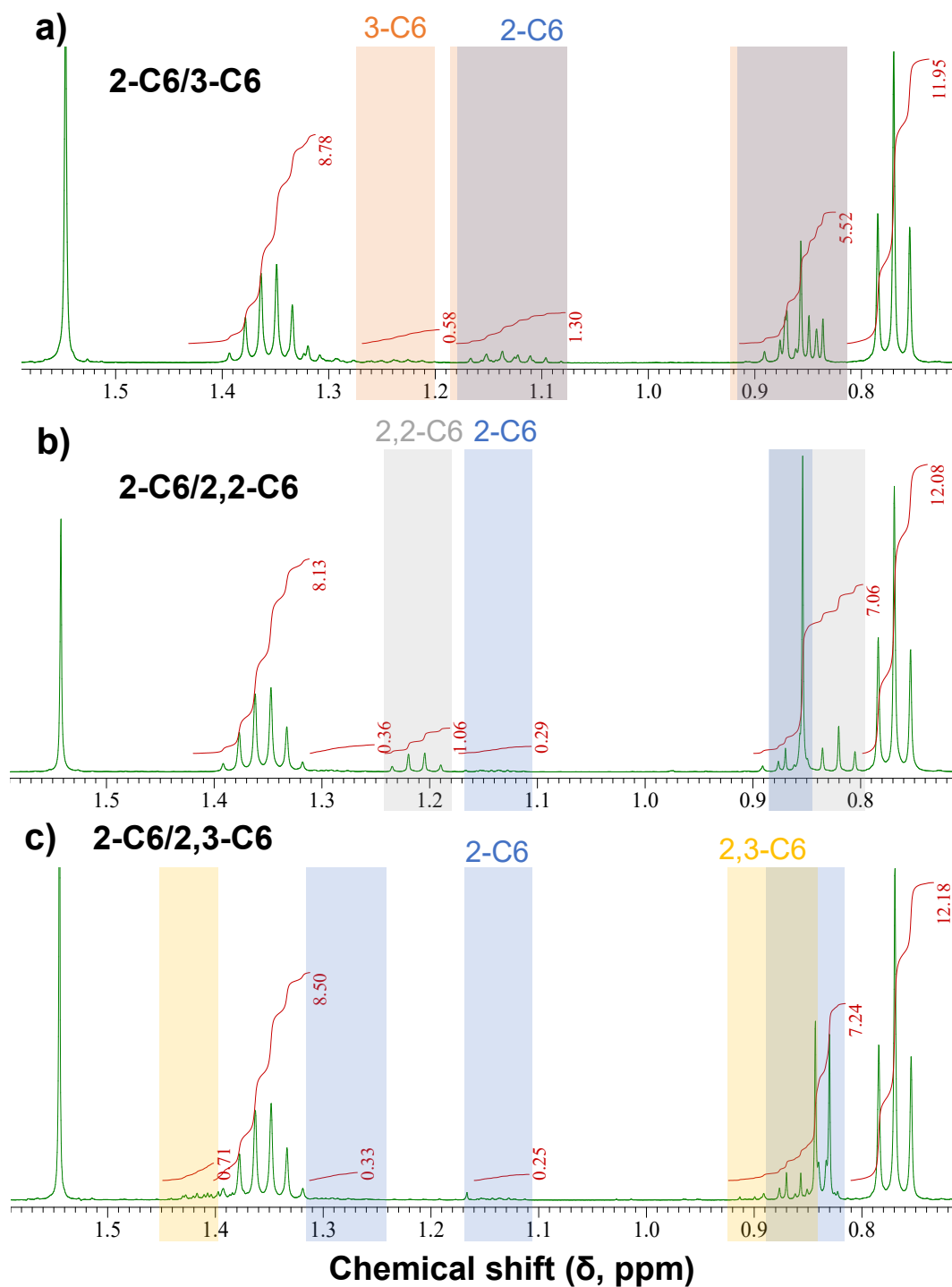


Fig. S10 500 MHz ^1H NMR spectra (δ from TMS, CDCl_3) after exposure of **1a** with 2-C6 and branched alkane mixed vapors as each two-component system. a) **1a** exposed to 2-C6/3-C6, b) **1a** exposed to 2-C6/2,2-C6, and c) **1a** exposed to 2-C6/2,3-C6. The colored areas on the spectra indicate the regions where the respective chemical shifts of the C6 alkanes appear. The color codes: pale blue = 2-C6; pale orange = 3-C6; pale gray = 2,2-C6; pale yellow = 2,3-C6.

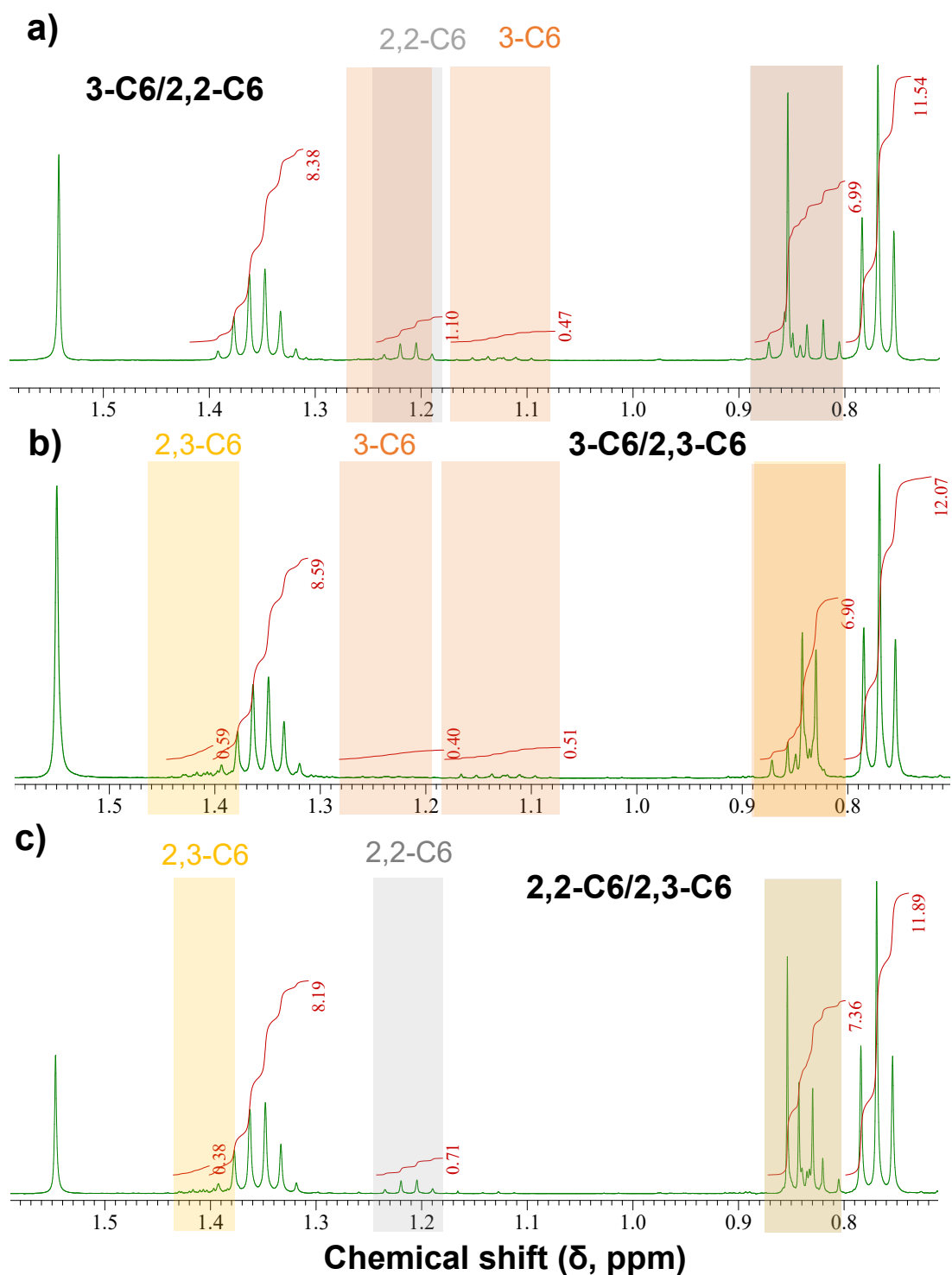


Fig. S11 500 MHz ^1H NMR spectra (δ from TMS, CDCl_3) after exposure of **1a** with branched alkane mixed vapors as each two-component system. a) **1a** exposed to 3-C6/2,2-C6, b) **1a** exposed to 3-C6/2,3-C6, and c) **1a** exposed to 2,2-C6/2,3-C6. The colored areas on the spectra indicate the regions where the respective chemical shifts of the C6 alkanes appear. The color codes: pale orange = 3-C6; pale gray = 2,2-C6; pale yellow = 2,3-C6.

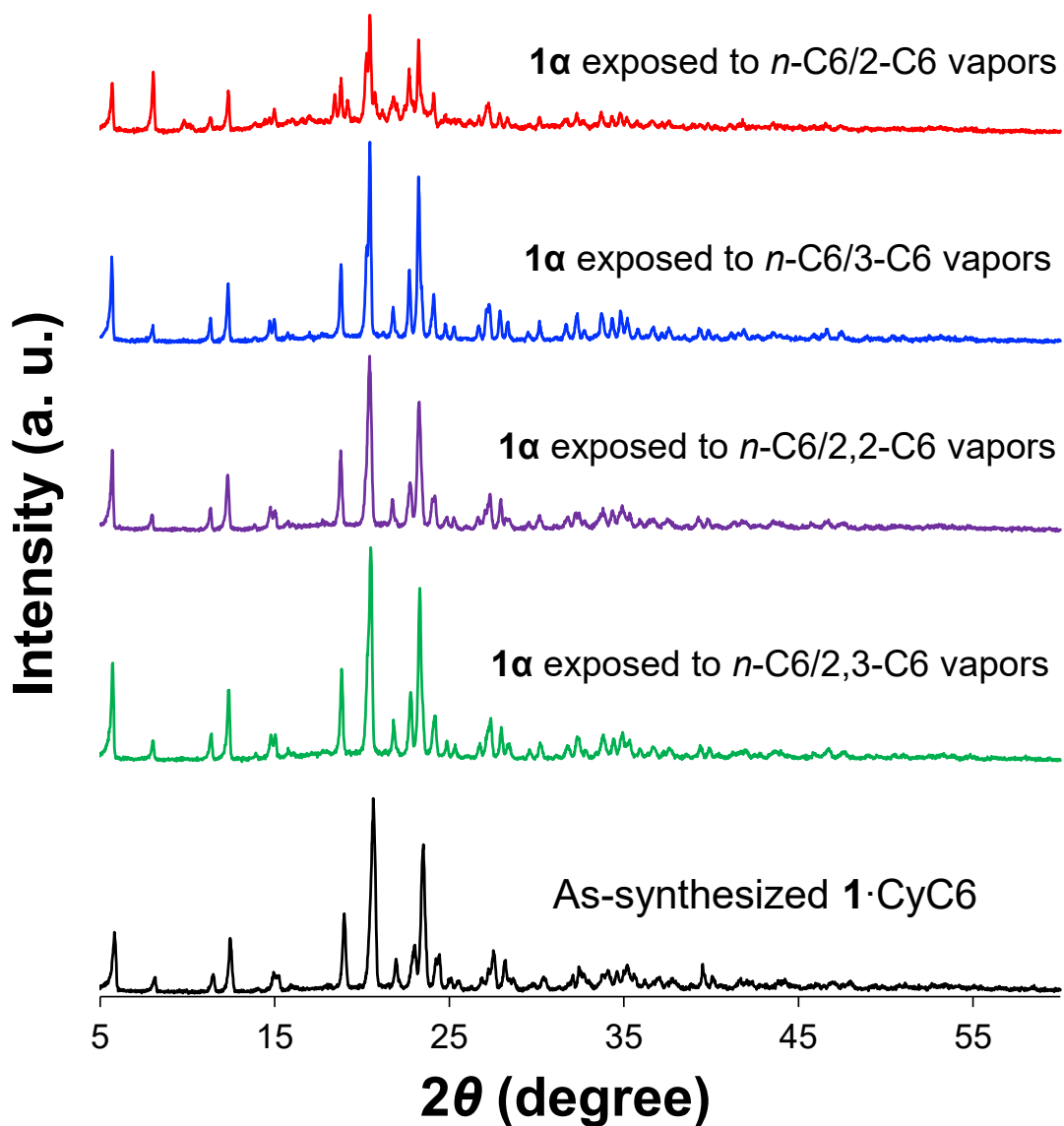


Fig. S12 PXR D patterns of **1α** exposed to *n*-C6/2-C6 (red line), *n*-C6/3-C6 (blue line), *n*-C6/2,2-C6 (purple line), *n*-C6/2,3-MeCyC6 (green line) vapors as a two-component system, and as-synthesized **1·CyC6** (black line).

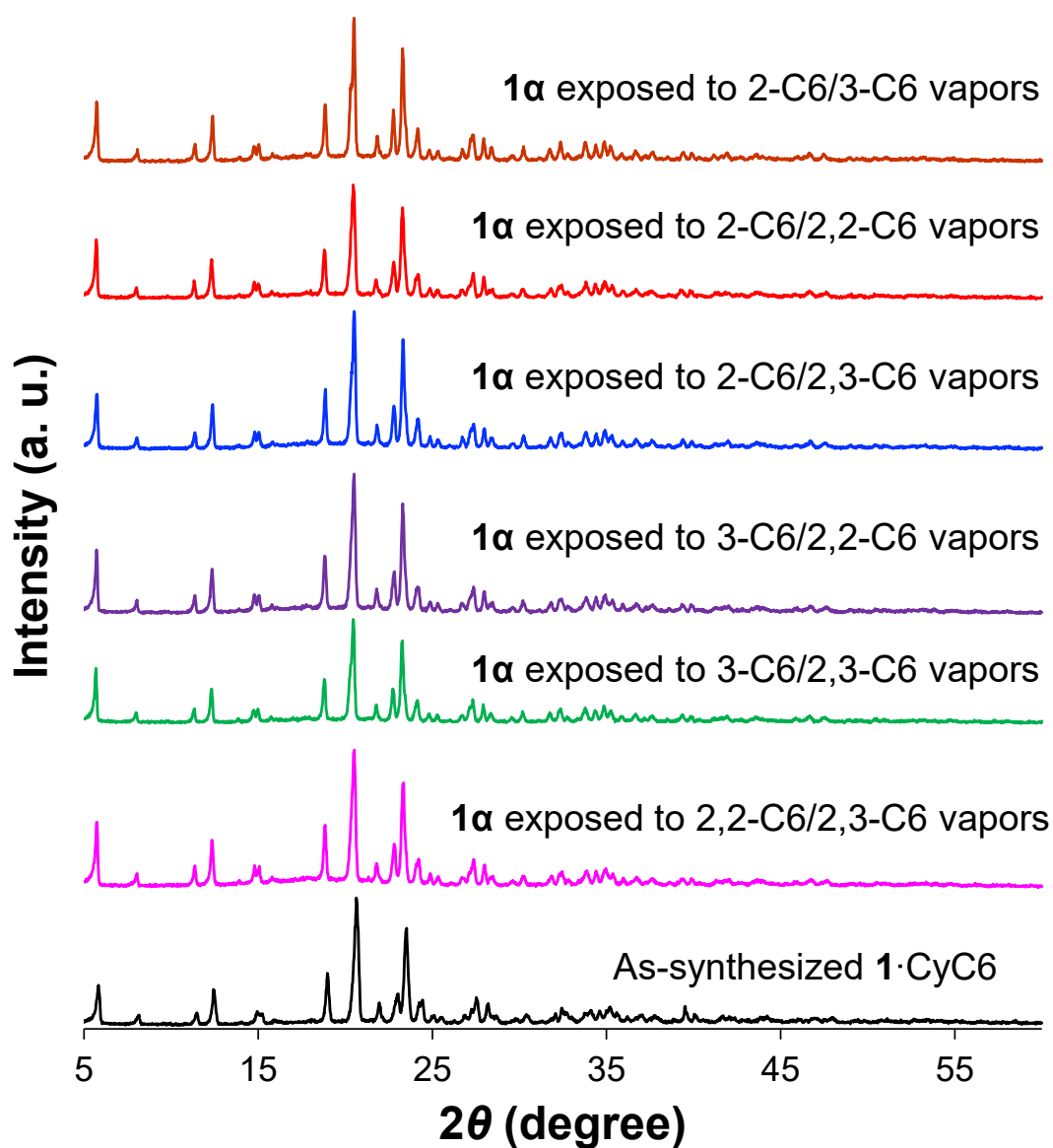


Fig. S13 PXR D patterns of **1α** exposed to 2-C6/3-C6 (brown line), 2-C6/2,2-C6 (red line), 2-C6/2,3-C6 (blue line), 3-C6/2,2-C6 (purple line), 3-C6/2,3-C6 (green line), 2,2-C6/2,3-C6 (pink line) vapors as a two-component system, and as-synthesized **1·CyC6** (black line).

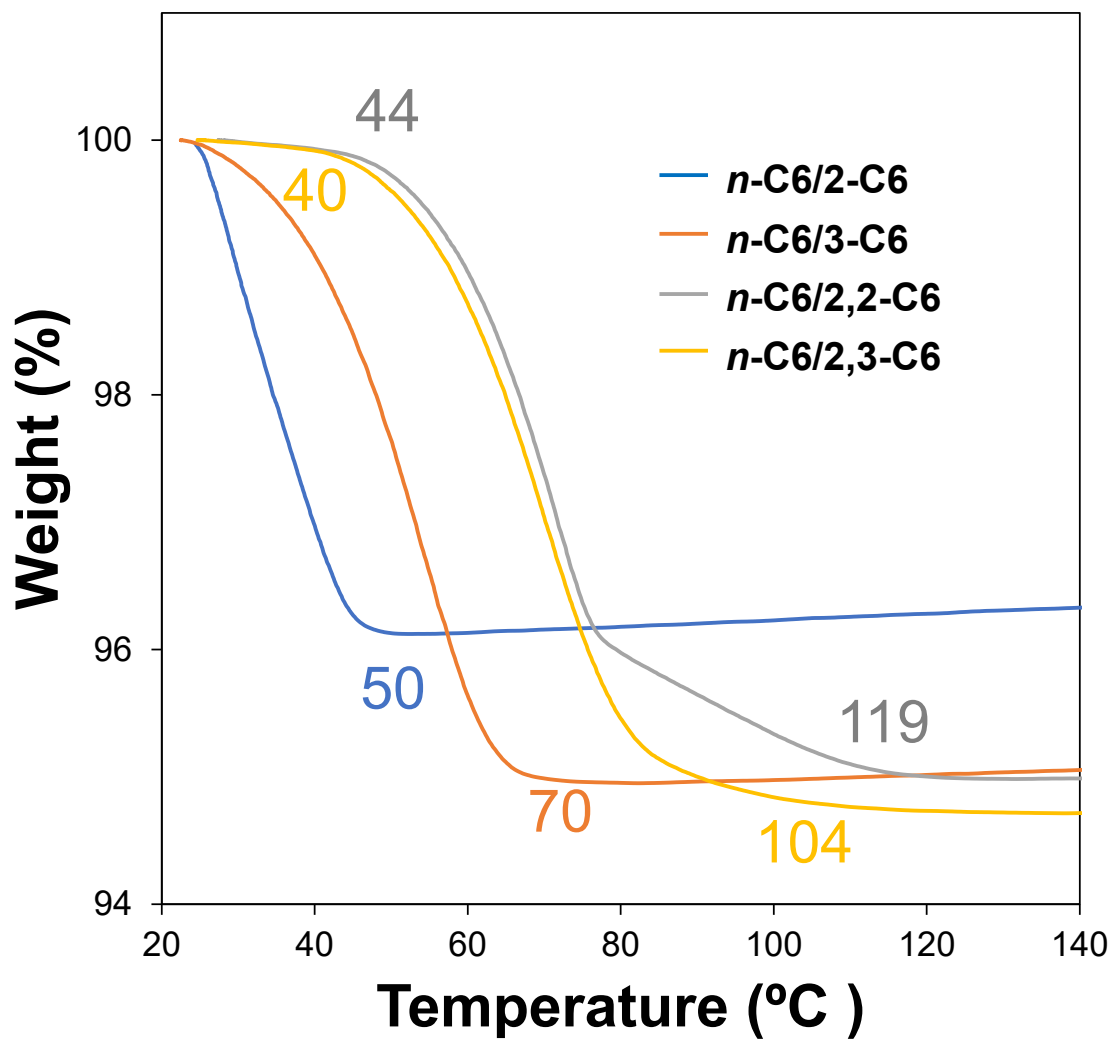
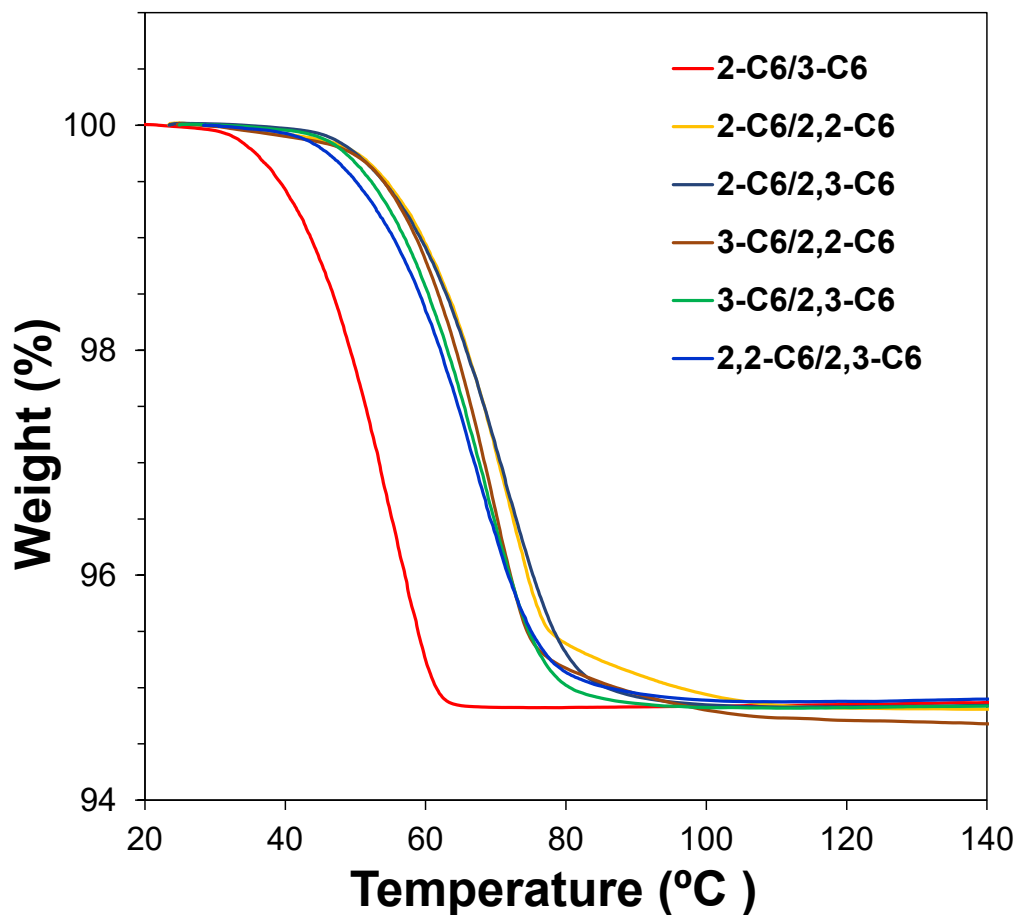


Fig. S14 Thermogravimetric analysis (TGA) of *n*-C6/2-C6 (blue line), *n*-C6/3-C6 (orange line), *n*-C6/2,2-C6 (gray line), and *n*-C6/2,3-C6 (yellow line) adsorbed in **1a**.



	Release start temperature (°C)	Release end temperature (°C)
2-C6/3-C6	30	63
2-C6/2,2-C6	48	105
2-C6/2,3-C6	44	89
3-C6/2,2-C6	46	104
3-C6/2,3-C6	42	86
2,2-C6/2,3-C6	40	100

Fig. S15 Thermogravimetric analysis (TGA) and release start and end temperature (in the table) of 2-C6/3-C6 (red line), 2-C6/2,2-C6 (yellow line), 2-C6/2,3-C6 (dark blue line), 3-C6/2,2-C6 (brown line), 3-C6/2,3-C6 (green line), and 2,2-C6/2,3-C6 (blue line) adsorbed in **1a**.

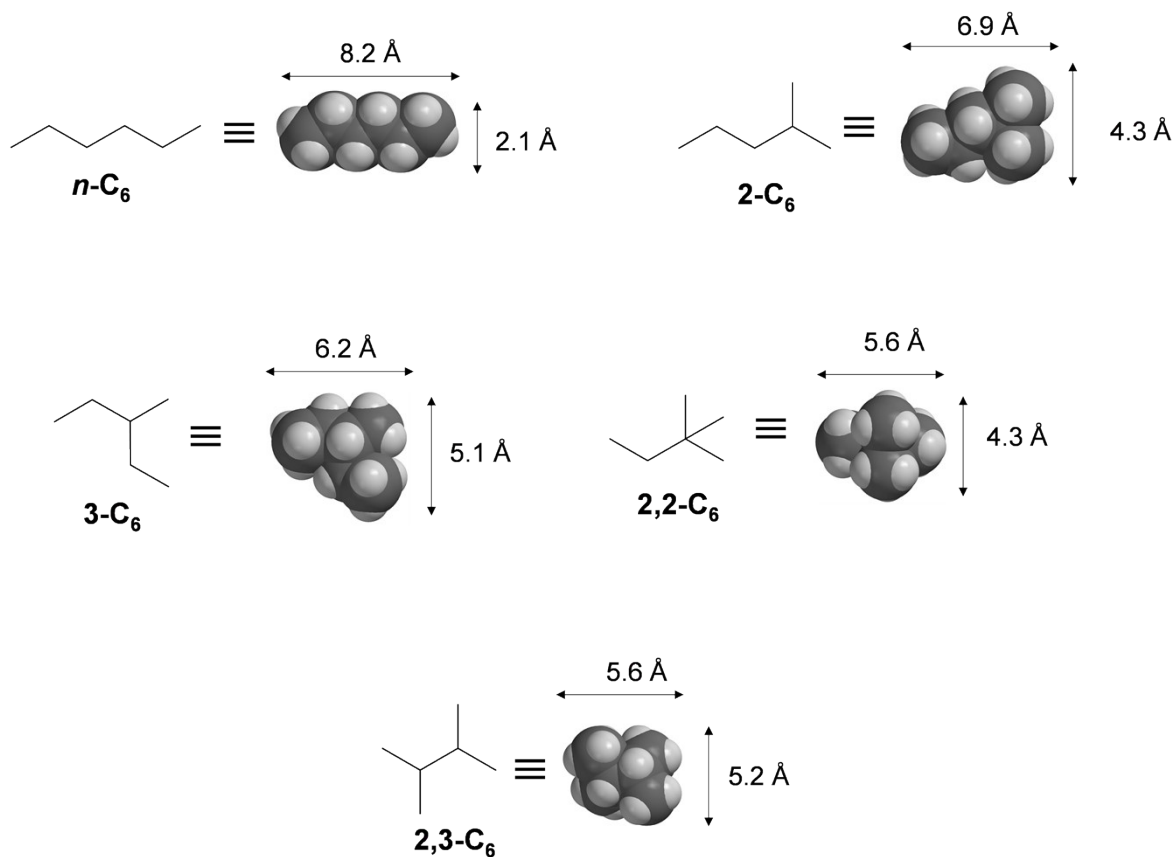


Fig. S16 Molecular size of the three types of C₆ alkanes calculating by ω B97X-D functional with 6-31G* basis set using Spartan '16 software (version 2.0.7).^{S3}

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- S1 F. Hamada, M. Yamada, Y. Kondo, S. Ito and U. Akiba, *CrystEngComm*, **2011**, *13*, 6920-6923.
- S2 M. Yamada, F. Uemura, U. M. R. Kunda, T. Tanno, H. Katagiri and F. Hamada, *Chem. Eur. J.* **2020**, *26*, 8393–8399.
- S3 Spartan 16™, Wavefunction Inc., Irvine, CA, USA, 2016.