Electronic Supplementary Information

Holding of Planar Chirality of Pillar[5]arene by Kinetic Trapping Using Host-Guest Interactions with Achiral Guest Solvents

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1. Materials

All solvents and reagents were used as supplied. Pillar[5]arene with 2-(*S*)-methylbutoxy groups at both rims **1** was synthesized according to the previous paper.[S1]

2. Methods

2.1 Solution NMR

Solution ^{1}H NMR spectra were recorded at 500 MHz with a JEOL-ECA500 spectrometer.

2.2 UV-Vis Absorption and CD Measurements

UV-Vis Absorption and circular dichroism spectra were recorded with a JASCO V-670 and J-1500, respectively. For UV-Vis absorption and CD measurements, 2 mm and 1 cm quartz cuvets were used, respectively. To measure CD spectra of **1** in various halogenated solvents after reaching the equilibrium state, the solutions of **1** were measured after dissolving **1** in these solvents for 168 h at 25 °C. To monitor the CD changes at 310 nm, we dissolved **C2Cl**-solvated and desolvated solids **1** in solutions, waited for 5 minutes at 25 °C, then started monitoring of the CD change in order to measure under the same conditions. To change the measurement temperature during monitoring CD changes at 310 nm, we stopped the monitoring, then changed the measurement temperature, waited for 5 minutes to make the measurement temperature constant, then started the monitoring at the target temperature.

2.3 Optical Rotations

Optical rotations were measured with a JASCO P2300. One hundred millimeter quartz cylindrical cell was used.

3. Sample Preparations

3.1 Preparation of C2Cl-solvated Solid 1

The solid **1** was dissolved in **C2Cl**. Then, the evaporation of **C2Cl** afforded the solid **1**. The resulting solid was dried under reduced pressure at 25 °C for 24 h to obtain **C2Cl**-solvated solid **1**.

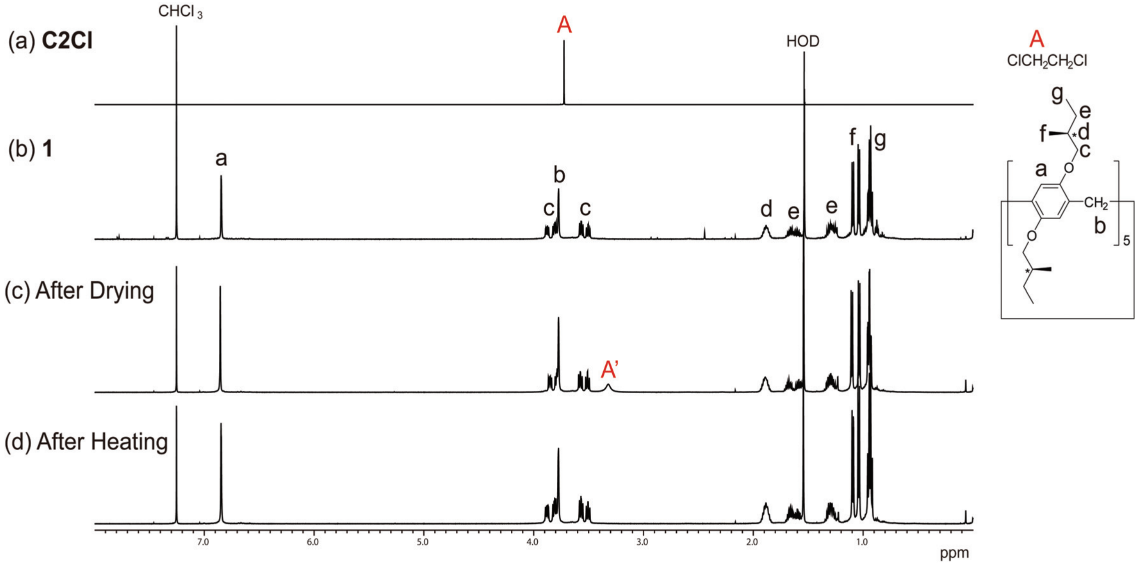


Fig. S1 ^{1}H NMR spectra ($CDCl_3$, 25 °C) of (a) **C2Cl**, (b) **1**, (c) the solid after drying at 25 °C, and (d) the solid after heating at 150 °C for 20 min.

The sample after drying at 25 °C showed new broadening peak (**Fig. S1c**, A'), which corresponding to proton signal of **C2Cl** included into pillar[5]arene cavity of **1**. The result indicates formation of **C2Cl**-solvated solid **1** after drying at 25 °C.

3.2 Preparation of Desolvated Solid 1

The **C2Cl**-solvated solid **1** was heated at 150 °C for 20 min. After heating, the solid was dried under reduced pressure at 25 °C for 24 h to obtain desolvated solid **1**.

The peak from proton signal of **C2Cl** included into pillar[5]arene cavity of **1** (A' in **Fig. S1c**) disappeared after the heating (**Fig. S1d**), indicating desolvation of **C2Cl** solvent guest from the solid **1**.

3.3 Single Crystals of C2Cl@1 Complex

Pillar[5]arene **1** was dissolved in mixture of chloroform and **C2Cl**, then methanol was added. Single crystals of **C2Cl@1 complex** were grown from the mixture.

3.4 Single Crystals of C4Br@1 Complex

Pillar[5]arene **1** was dissolved in mixture of chloroform and **C4Br**, then methanol was added. Single crystals of **C4Br@1 complex** were grown from the mixture.

4. UV-Vis Spectra

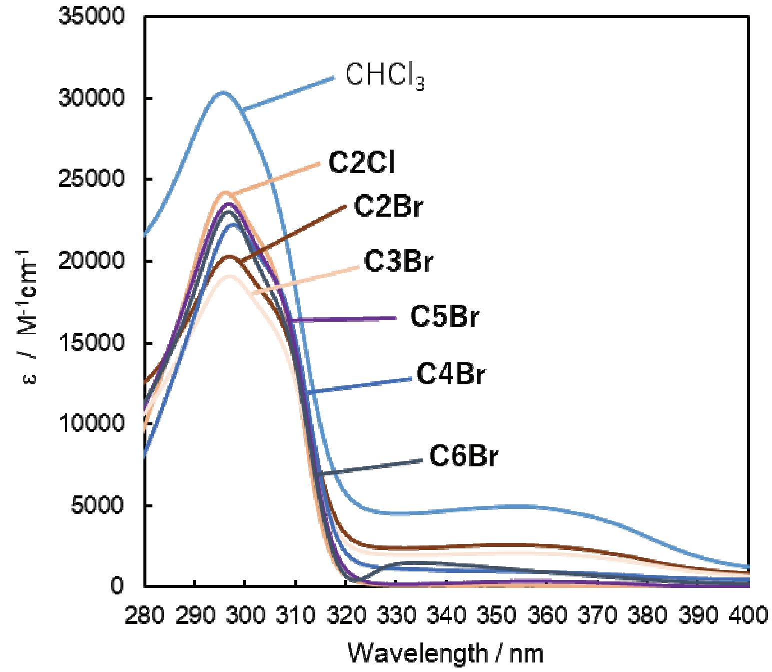
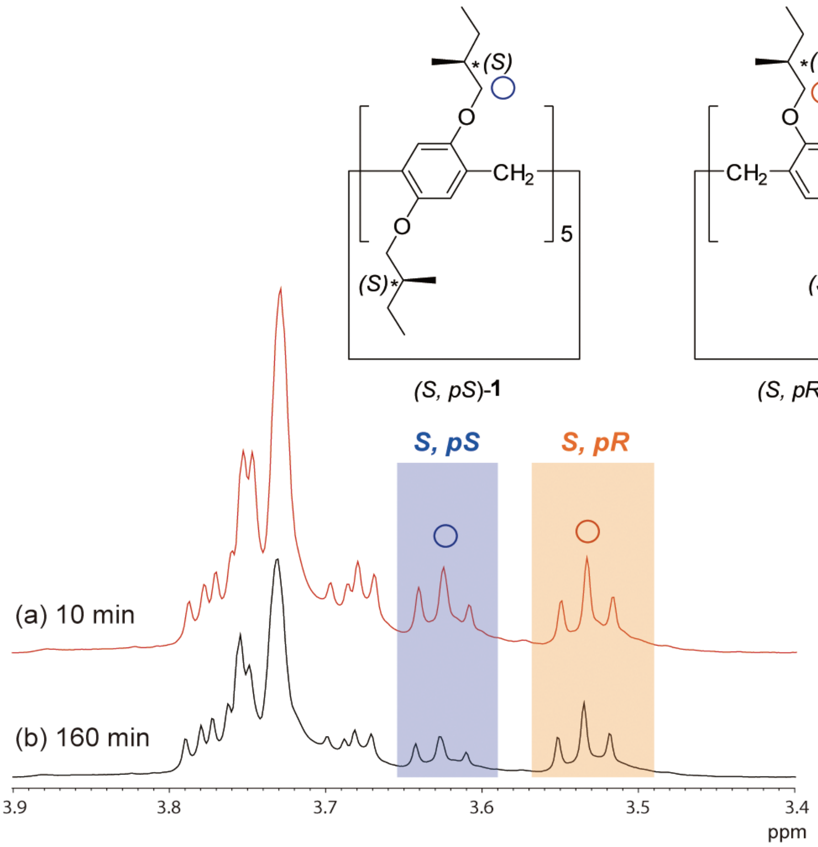


Fig. S2 UV-Vis spectra (25 °C, 0.1 mM) of the solutions **1** in $CHCl_3$, **C2Cl**, **C2Br**, **C3Br**, **C4Br**, **C5Br** and **C6Br**. The broad transition at 350-360 nm may result from the through-space π-delocalization between 1,4-dialkoxybenzene units because the rotation speed of the units would change depending on the kinds of solvents. In addition, phosphorescence was reported from 1,4-dialkoxybenzene derivatives by formation of H-aggregate structures.[S2] Therefore, arrangement of 1,4-dialkoxybenzene units would result in the broad transition at 350-360 nm.

5. Monitoring Diastereomeric Excess Change by ^{1}H NMR



(c) Time-dependent d.e.% change

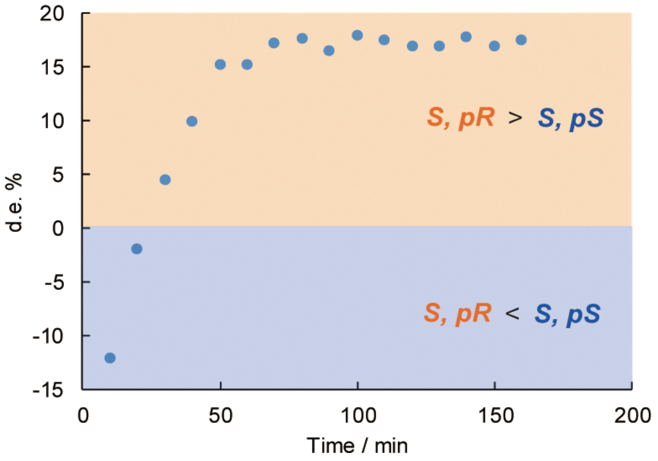


Fig. S3 ^{1}H NMR spectra (25 ºC) of the solution **1** by keeping at 25 ºC for (a) 10 min. and (b) 160 min. after dissolving the desolvated solid **1** in CD_2ClCD_2Cl. (c) Diastereomeric excess change depending on the time by monitoring ^{1}H NMR.

6. Monitoring CD Changes in Linear Halogenated Solvents

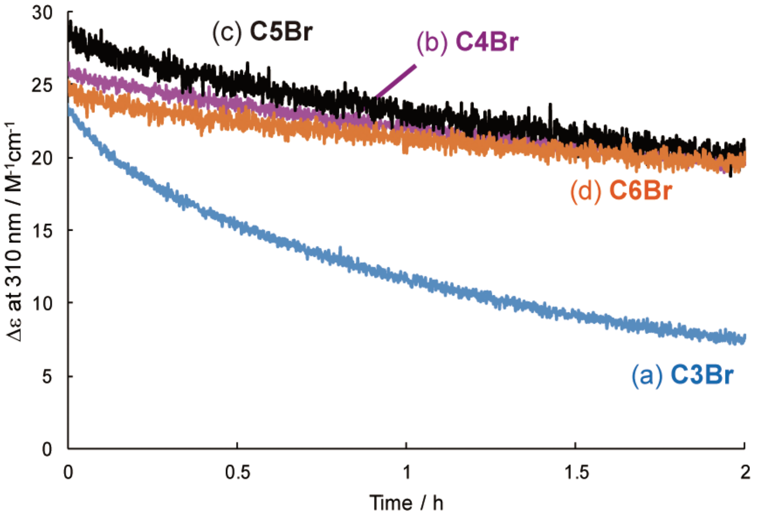
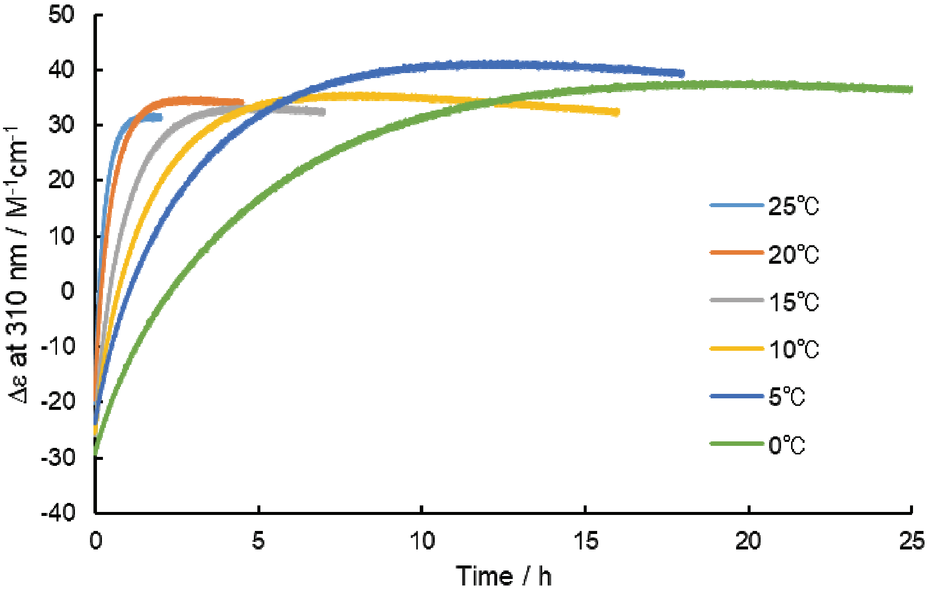


Fig. S4 CD changes at 310 nm of the solutions **1** (0.1 mM, 25 ºC) after dissolving the **C2Cl**-solvated solid **1** in (a) **C3Br** (blue line), (b) **C4Br** (purple line), (c) **C5Br** (black line) and (d) **C6Br** (orange line).

The CD signal change in **C3Br** (**Fig. S4a**) was slower than in **C2Cl** (**Fig. 3b**). When we used longer **C4Br** (**Figs. S4b** and **3c**), **C5Br** (**Fig. S4c**) and **C6Br** (**Fig. S4d**) as a solvent, the positive CD signal hardly change by keeping the sample at 25 ºC for 2 h. Therefore, by using **C4Br**, **C5Br** and **C6Br** as a solvent, we successfully held the planar-chiral information of the **C2Cl**-solvated solid **1** for a given length of time.

7. Eyring Plots

(I)



(II)

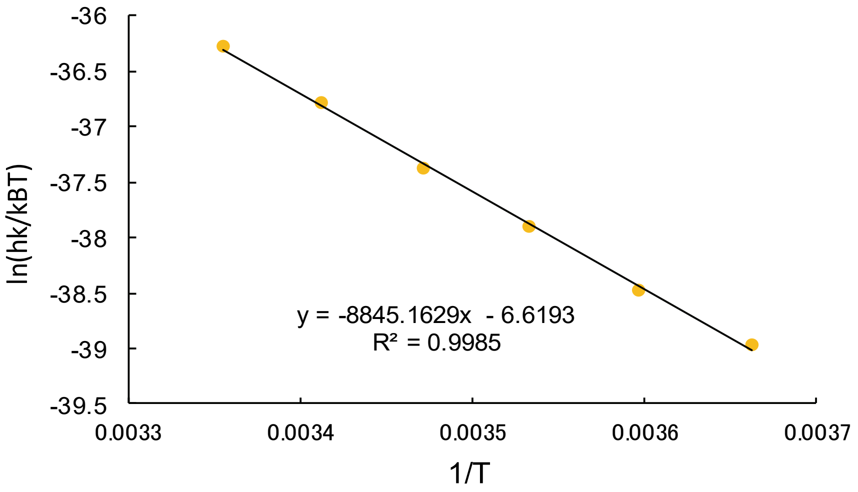
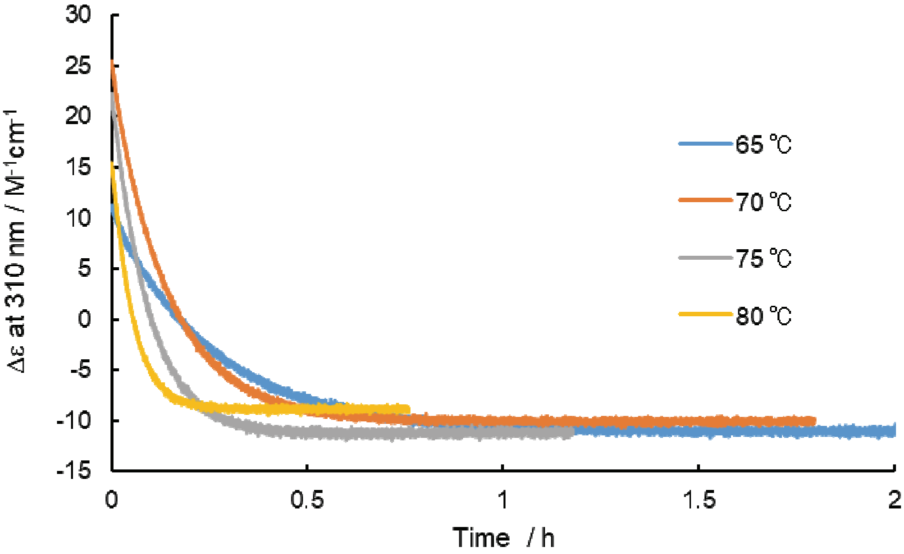


Fig. S5 (I) CD changes at 310 nm of the solutions **1** (0.1 mM) at various temperatures after dissolving the desolvated solid **1** in **C2Cl**. (II) Eyring plots from the CD changes.

(I)



(II)

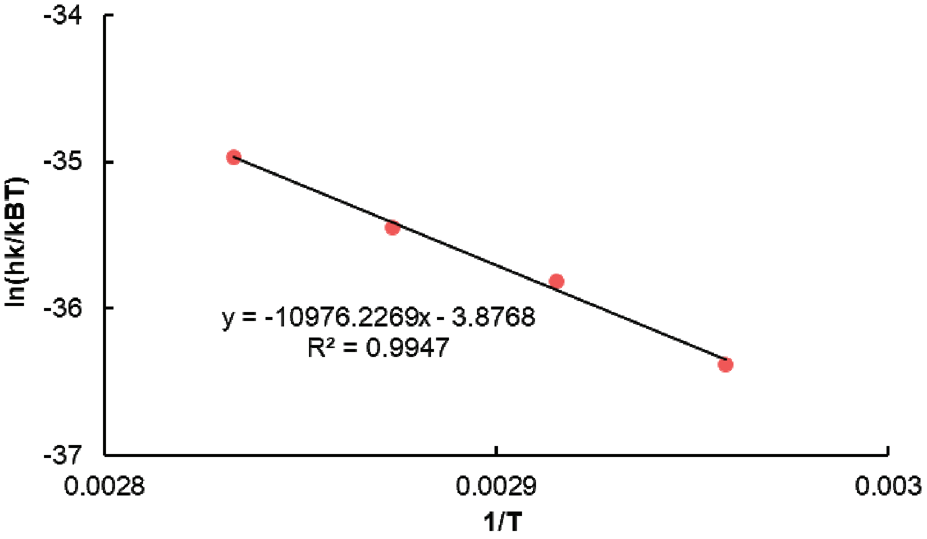
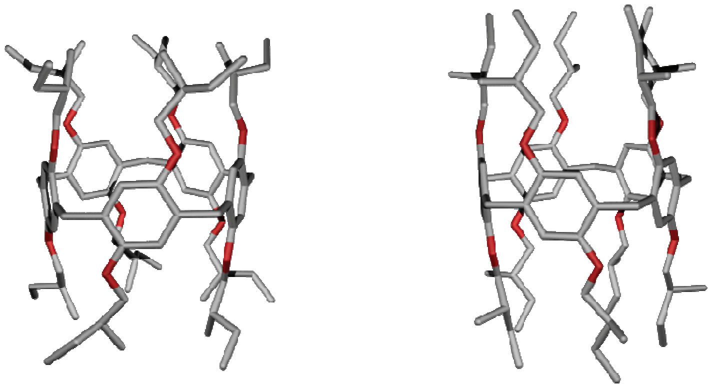


Fig. S6 (I) CD changes at 310 nm of the solutions **1** (0.1 mM) at various temperatures after dissolving the desolvated solid **1** in **C4Br**. (II) Eyring plots from the CD changes.

8. Computational Details

The geometries of (*S*, *pS*)-**1** and (*S*, *pR*)-**1** were optimized at ωB97XD/6-31G(d,p) level, and their heats of formation were calculated after including zero point vibrational energy correction using Gaussian 16 (ES64L-G16 RevC.01).[S3] (*S*, *pS*)-**1** was found to be 14.8 kJ/mol (3.5 kcal/mol) more stable than (*S*, *pR*)-**1**. The optimized structures of (*S*, *pS*)-**1** and (*S*, *pR*)-**1** with their heats of formation are shown in **Fig. S7**.



(*S*, *pS*)-1
-10677447.39 kJ/mol

(*S*, *pR*)-1
-10677432.57 kJ/mol

Fig. S7 The optimized structures of (*S*, *pS*)-**1** and (*S*, *pR*)-**1** with their heats of formations. (*S*, *pS*)-**1** was 14.8 kJ/mol (3.5 kcal/mol) more stable than (*S*, *pR*)-**1**.

9. References

S1) T. Ogoshi, R. Shiga, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.,* 2011, **76**, 618.
S2) Z. An, C. Zheng, Y. Tao, R. Chen, H. Li, R. Deng, X. Liu and W. Huang, *Nat. Mater.,* 2015, **14**, 685.
S3) Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.