**Electronic Supplementary Information (ESI)**

Diastereoselective Synthesis of a [2]Catenane from a

Pillar[5]arene and a Pyridinium Derivative

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**Table of Contents**

<table>
<thead>
<tr>
<th>Section/Reference</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental section</td>
<td>S2-S3</td>
</tr>
<tr>
<td>Figs. S1-S4 ¹H and ¹³C NMR spectra</td>
<td>S4-S7</td>
</tr>
<tr>
<td>Fig. S5 ¹H NMR spectrum of 1:1 mixture of 1 and pillar[5]arene 2</td>
<td>S8</td>
</tr>
<tr>
<td>Fig. S6 ¹H NMR titration</td>
<td>S9</td>
</tr>
<tr>
<td>Fig. S7 Computationally generated energy-minimized molecular model of [2]catenane 3</td>
<td>S10</td>
</tr>
<tr>
<td>Reference</td>
<td>S11</td>
</tr>
</tbody>
</table>
Experimental section

Materials. All solvents and reagents were used as supplied. per-Ethylated pillar[5]arene 2 was synthesized according to the previous paper.\textsuperscript{S1}

Measurements. The $^1$H NMR spectra were recorded at 500 MHz and $^{13}$C NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. Chiral HPLC experiments were performed on a Waters Delta 600 pump and 600E Controller with a dual 2489 UV/Vis detector.

Pyridinium derivative 1.
A mixture of 4-hydroxypyridine (250 mg, 2.63 mmol), 18-bromo-1-octadecene (1.05 g, 3.15 mmol) and K$_2$CO$_3$ (1.09 g, 7.89 mmol) in acetone (15 mL) was heated under reflux for 72h. The resulting solution was filtered and concentrated under reduced pressure. A mixture of the residue and 18-bromo-1-octadecene (1.05 g, 3.15 mmol) in acetonitrile was heated under reflux for 48h. The resulting precipitate was isolated by filtration. The washing of the solid with cold acetonitrile and diethyl ether afforded 1 (1.20 g, 1.77 mmol, Yield: 67%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 9.09 (d, 2H), 7.42 (d, 2H), 5.77-5.85 (m, 2H), 4.92-5.01 (m, 4H), 4.70 (t, 2H), 4.28 (t, 2H), 1.84-2.06 (m, 8H), 1.24-1.48 (m, 52H). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm): $\delta$ 170.3, 146.4, 139.3, 114.1, 114.0, 71.6, 60.2, 33.9, 31.7, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.0, 28.5, 26.1, 25.7. HRMS (ESI): m/z Calcd for C$_{41}$H$_{74}$NO $[^{[M-Br-]+}]$: 596.57649, found 596.58682.

A solution of 1 (50.0 mg, 0.0739 mmol) and pillar[5]arene 2 (6.58 g, 7.38 mmol) in chloroform (148 mL) was degassed via a freeze-pump-thaw method. Under a nitrogen atmosphere, Grubbs first generation catalyst (benzylidene-bis(tricyclohexylphosphine)-dichlororuthenium, 30.3 mg, 0.0368 mmol) was added, and stirring was continued at 25 °C for 24h. The resulting solution was concentrated under reduced pressure. Column chromatography (silica gel; DCM : MeOH = 96 : 4) afforded [2]catenane 3 (26.8 mg, 0.0174 mmol, Yield: 24%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.21 (d, 2H), 6.95 (s, 5H), 6.72 (s, 5H), 6.25 (d, 2H), 5.29-5.36 (m, 2H), 4.29-4.45 (m, 2H), 3.65-4.03 (m, 30H), 1.81-1.99 (m, 6H), 1.26-1.50 (m, 78H), 0.74-0.96 (m, 4H), -0.05 (m, 2H), -0.99 (m, 2H). $^{13}$C NMR (CDCl$_3$, 125MHz, ppm): $\delta$ 169.5, 150.4, 149.5, 144.1, 130.7, 129.9, 129.2, 116.1, 115.1, 112.9, 72.4, 65.5, 64.1, 57.4, 32.9, 30.9, 30.2, 30.1, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.1, 28.7,
28.2, 27.8, 26.7, 25.6, 15.6, 15.5. HRMS (FAB): m/z Calcd for C94H140NO11 [M-Br]⁺: 1459.04209, found 1459.0432.

**Determination of association constant.** ¹H NMR titrations were done with solutions which had a constant concentration of guest (1 mM) and varying concentrations of host. By the non-linear curve-fitting methods, the association constant for 1-2 complex in CDCl₃ was determined to be (1.76 ± 0.19) × 10³ M⁻¹ for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:

\[
\Delta \delta_{\text{obs}} = \frac{\Delta \delta_{11}}{2K[G]_0} \left[1 + K[H]_0 + K[G]_0 - \{(1 + K[H]_0 + K[G]_0)^2 - 4K^2[H]_0[G]_0\}^{1/2}\right]
\]

Where \(\Delta \delta_{\text{obs}}\) is the chemical shift change of proton signal of guest at \([H]_0\), \(\Delta \delta_{11}\) is the chemical shift change of the guest proton resonance when the host is completely complexed, \([G]_0\) is the fixed initial concentration of the guest, and \([H]_0\) is the initial concentration of the host.
Fig. S1 $^1$H NMR spectrum of 1 in CDCl$_3$. 
Fig. S2 \(^{13}\text{C}\) NMR spectrum of 1 in CDCl\(_3\).
Fig. S3 $^1\text{H}$ NMR spectrum of [2]catenane 3 in CDCl$_3$. 
\[ ^{13}\text{C} \text{ NMR spectrum of [2]catenane 3} \]

Fig. S4 \[ ^{13}\text{C} \text{ NMR spectrum of [2]catenane 3 in CDCl}_3. \]
$^1$H NMR spectrum of 1:1 mixture of 1 and pillar[5]arene 2

Fig. S5 $^1$H NMR spectra (5 mM) of (a) pillar[5]arene 2, (b) 1:1 mixture of 1 and 2, and (c) 1 in CDCl$_3$ at 25 °C.
$^1$H NMR Titration

$K = 1800 \pm 190 \text{ M}^{-1}$

$R^2 = 0.99922$

**Fig. S6** $^1$H NMR titration curves CDCl$_3$, 25 °C) of the pyridinium proton (proton b in **Fig. 2c**); [1] = 1 mM, [2] = 0-7 mM.
**Computationally Generated Energy-Minimized Molecular Model of [2]Catenane 3**

![Computationally Generated Energy-Minimized Molecular Model of [2]Catenane 3](image)

**Fig. S7** Computationally generated energy-minimized molecular model of [2]catenane 3 by DFT calculations (B3LYP/3-21G). The alkyl chain of the pyridinium wheel in 3 is tightly included in cavity of pillar[5]arene 2 in 3, thus conformation of pillar[5]arene units of 2 in [2]catenane 3 is immobilized.
Reference