Electronic Supplementary Information

Face selective translation of a cyclodextrin ring along an axle

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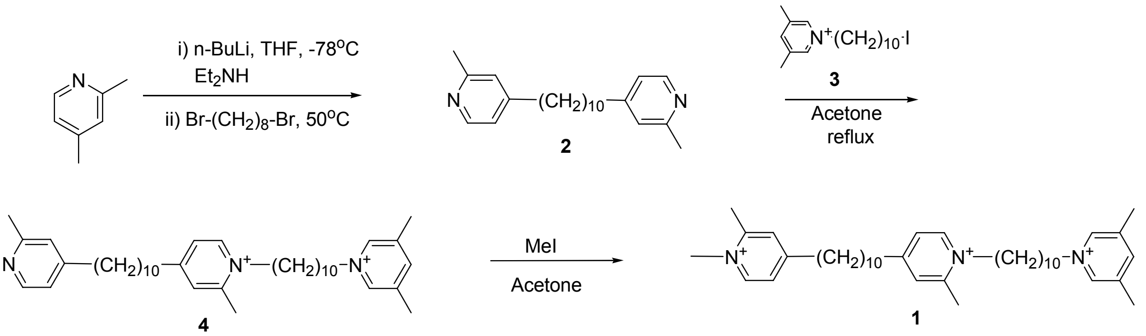
I. Synthetic experimental procedures

Materials

α-CD was obtained from Nacalai Tesque Inc. and used after recrystalization and drying at 80°C under vacuum. 2-Picoline, 2,4-lutidine, diethylamine, methyl iodide, and hydrobromic acid were obtained from Nacalai Tesque Inc. 3,5-Lutidine, 1,8-dibromooctane, and 1,10-diiodododecane obtained from Tokyo Kasei Kogyo Co. Ltd. *n*-Butyllithium was obtained from Kanto Chem. Co.

Axle molecules were synthesized as follows.

Scheme S1



2: Under Ar atmosphere, distilled 2,4-lutidine (1.0 mL, 8.6 mmol) was dissolved in distilled THF (30 mL). Hexane solution of *n*-buthyllithium (1.56 M, 6 mL) was added to the solution at -78°C. After stirring for 30 minutes, distilled diethyl amine (1.5 mL) was added to the solution. After stirring for 1 hour, dry 1,8-dibromooctane (800 μL, 4.3 mmol) was added to the solution, then the solution was heated gradually to 50°C and stirred overnight. Aqueous solution of ammonium chloride (0.5 N, 10mL) was added to the solution to quench the reaction. The solution was extracted with diethyl ether, then organic phase was evaporated after the dried by sodium sulfate. The residue was dissolved in methanol and poured into hexane. The precipitation was filtered off, then the solvent was evaporated to give 487.7 mg (35 %) of **5** as yellow oil. ^{1}H-NMR (500 MHz, DMSO-d_6) δ 8.66-8.67 (d, 2H), 7.81 (s, 2H), 7.74-7.75 (dd, 2H), 2.79-2.82 (t, 4H), 2.67 (s, 6H), 1.60-1.66 (m, 4H), 1.20-1.39 (m, 12H).

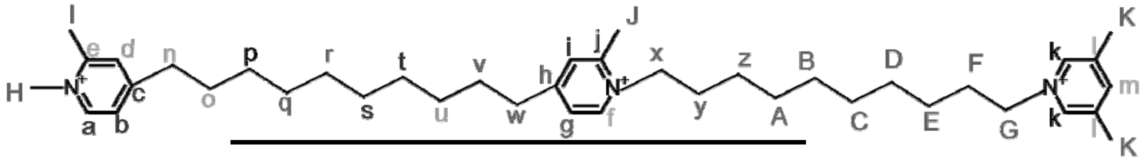
3: The acetonitrile (20 mL) solution of 3,5-lutidine (360 μL, 3.6 mmol) and 1,10-diododecane (14 g, 36 mmol) was stirred for overnight under reflux. The solution was poured into diethyl ether to give 1.4 g (79 %) of **6** as yellow solid. ^{1}H-NMR (500 MHz, DMSO-d_6) δ 8.84 (s, 2H), 8.29 (s, 1H), 4.46-4.50 (t, 2H), 3.23-3.29 (t, 2H), 2.45 (s, 6H), 1.86-1.95 (m, 2H), 1.69-1.76 (m, 2H), 1.23-1.33 (m, 12H).

4: The acetone solution (7 mL) of **5** (375 mg, 0.849 mmol) and **6** (84.9 mg, 0.168 mmol) was stirred under reflux for 4 days. The solution was poured into diethyl ether, and the precipitate was collected and reprecipitate from methanol to diethyl ether to give 130 mg (92.9 %) of **7** as brown oil. ^{1}H-NMR (500 MHz, DMSO-d_6) δ 8.80-8.81 (d, 1H), 8.79 (s, 2H), 8.29 (s, 1H), 8.29-8.28 (d ,1H), 7.90 (s, 1H), 7.81-7.82 (d ,1H), 7.05 (s, 1H), 6.98-6.99 (d ,1H), 4.44-4.47 (t, 2H), 4.41-4.45 (t, 2H), 2.77-2.80 (t, 4H), 2.76 (s, 3H), 2.50 (s, 6H), 2.40 (s, 3H), 1.84-1.93 (m, 2H), 1.75-1.83 (m, 2H), 1.58-1.68 (m, 2H), 1.49-1.58 (m, 2H), 1.13-1.35 (m, 24H).

1: Methyl iodide (1.0 mL, 16 mmol) and **7** (55 mg, 0.067 mmol) were dissolved in acetone (10 mL), and the solution was stirred for 3 days at room temperature. The formed precipitate was collected and washed with diethyl ether to give 9.7 mg (15 %) of **1** as yellow oil. ^{1}H-NMR (500 MHz, D_2O) δ 8.41-8.45 (m, 2H), 8.41 (s, 2H), 8.10 (s, 1H), 7.66 (s, 2H), 7.56-7.61 (dd ,2H), 4.40-4.42 (t, 2H), 4.37-4.41 (t, 2H), 4.08 (s, 3H), 2.76-2.79 (t, 4H), 2.70 (s, 3H), 2.65 (s, 3H), 2.41 (s, 6H), 1.86-1.90 (m, 2H), 1.80-1.88 (m, 2H), 1.59-1.66 (m, 4H), 1.14-1.31 (m, 24H). ^{13}C-NMR (126 MHz, DMSO-d_6) see Table S1 in detail.

Anal. Calcd. for $(C_{40}H_{64}N_3I_3)_1(H_2O)_{1.00}$ C,48.74; H,6.75; N,4.26 Found: C,48.95; H,6.96; N,4.26

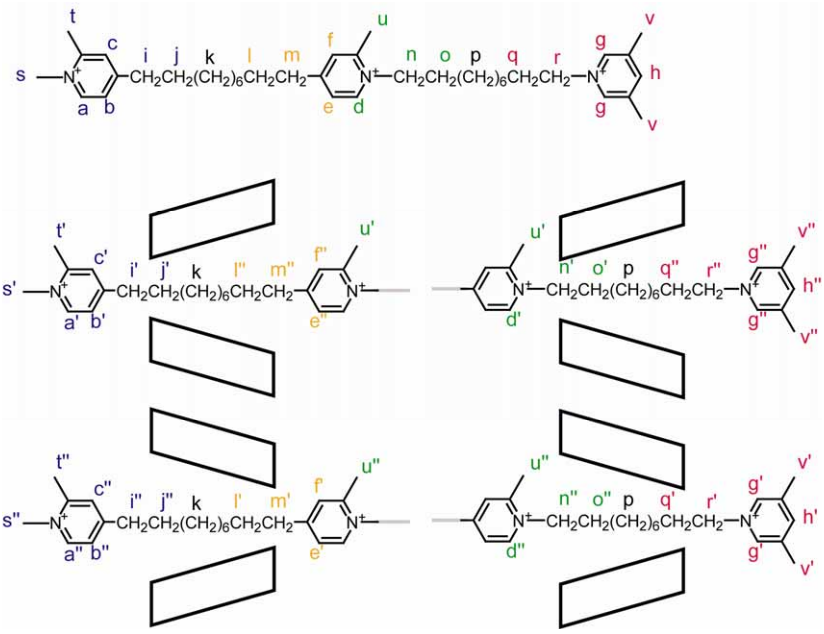
Table S1. Assignments of ^{13}C-NMR of **1**.



δ/ppm	carbon
162	h
162	d
155	j
154	e
146	m
145	f
144	a
141	l
138	k
129	i
128	b
125	g
125	d
60.4	G
56.5	x
44.6	H
34.4	n
34.4	w
30.5	F
29.4	y
29	o
29	v
28.9	r
28.9	s
28.8	C
28.7	B
28.6	q
28.6	t
28.5	p
28.5	u
28.4	D
28.3	A
25.4	E
25.4	z
19.7	J
19.3	I
17.7.	K

II. Assignment of resonance of 1-α-CD

Chart S1. Structure and the assignments of **1** and the complexes with α-CD.



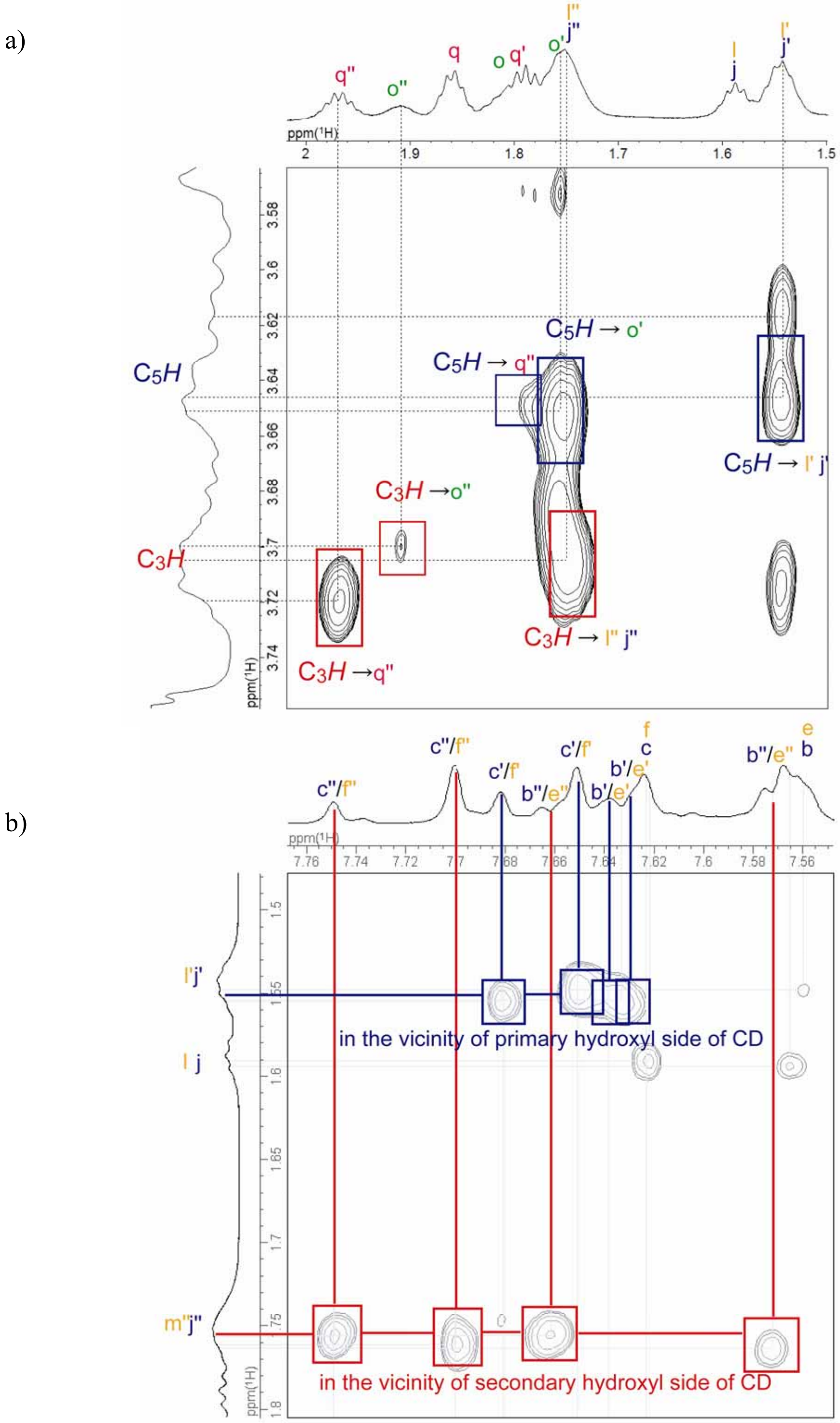


Figure S1. The partial ^{1}H-^{1}H ROESY spectra of **1** with α-CD in D_2O, 30°C at 920 MHz, mixing time = 150 ms. intermolecular correlations between α-CD and axle molecule (a) and intramolecular correlations between methylene part and pyridinium part of axle molecule (b). "x / y" means this signal derived from either proton x or y.

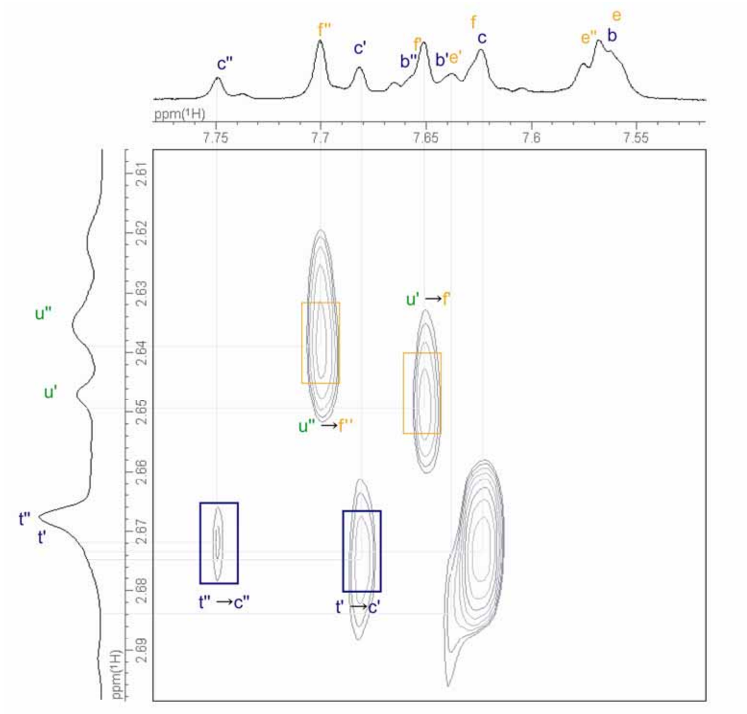
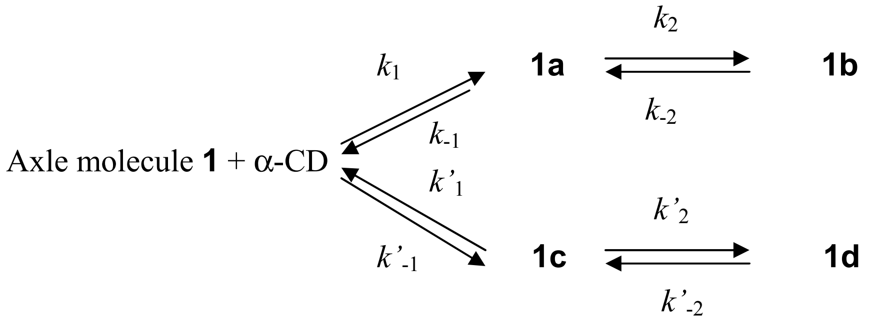


Figure S2. The partial ^{1}H-^{1}H ROESY spectra of **1** with α-CD in D_2O, 30°C at 920 MHz, mixing time = 150 ms. Intramolecular correlations between methyl part and pyridinium part of axle molecule

III. Kinetic study of α-CD with 1

The kinetic parameters for the threading of CD to the axle molecule **5** and for the translation between two stations were determined by fitting the plots in Figure 2 (see main text) to the following equations.



Here, we assume the reaction rate constants k_1, k_{-1}, k'_1, $k'_{-1} >> k_2$, k_{-2}, k'_2, k'_{-2}. Then, the molar concentrations [**1a**] and [**1c**] immediately reach to the steady state values $[1\mathbf{a}]_0$ and $[\mathbf{1c}]_0$ respectively, and the concentrations [**1b**] and [**1d**] should obey the following differential equations.

$$\begin{cases} \dfrac{d[1\mathbf{b}]}{dt} = k_2[1\mathbf{a}] - k_{-2}[1\mathbf{b}] \\ \dfrac{d[1\mathbf{d}]}{dt} = k'_2[1\mathbf{c}] - k'_{-2}[1\mathbf{d}] \end{cases}$$

By solving the equations under the initial conditions [**1b**] = [**1d**] = 0 at t = 0, we obtain the solutions.

$[\mathbf{1b}] = [\mathbf{1b}]_e(1-\exp(-k_2[\mathbf{1a}]_0 t/[\mathbf{1b}]_e))$

$[\mathbf{1a}]_0 k_2 = [\mathbf{1b}]_e k_{-2}$

$[\mathbf{1d}] = [\mathbf{1d}]_e(1-\exp(-k'_2[\mathbf{1c}]_0 t/[\mathbf{1d}]_e))$

$[\mathbf{1c}]_0 k'_2 = [\mathbf{1d}]_e k'_{-2}$

where $[\mathbf{1b}]_e$ and $[\mathbf{1d}]_e$ are [**1b**] and [**1d**] at t = ∞.

k_2, k_{-2}, k'_2 and k'_{-2} are described as $k_{(\mathbf{1a}\rightarrow\mathbf{1b})}$, $k_{(\mathbf{1b}\rightarrow\mathbf{1a})}$, $k_{(\mathbf{1c}\rightarrow\mathbf{1d})}$ and $k_{(\mathbf{1d}\rightarrow\mathbf{1c})}$, respectively in the main text.