Supporting Information for:

Chirality Rewriting Cycle Mediated by Dynamic Cyclen-Calcium Complex

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Materials and Instruments

Materials. Alkyne **3** and azide **4** were synthesized according to the reported method.[1,2] Starting materials and dehydrated solvents were purchased from Tokyo Chemical Industry (Tokyo, Japan), Wako Pure Chemical Industries (Osaka, Japan), Nakalai Tesque Inc. (Kyoto, Japan) and Sigma-Aldrich Co. (St. Louis, USA). Silica gel (SiO_2) for column chromatography was purchased from Merck (Darmstadt, Germany). Aluminium oxide (Al_2O_3, basic) for column chromatography was purchased from Wako Pure Chemical Industries (Osaka, Japan).

Instruments. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL lambda 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C, or a JEOL lambda 400 spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS) for ^1H and a deuterated solvent for ^{13}C, respectively. IR spectra were recorded on a PerkinElmer Spectum One FT-IR spectrometer. Absorption spectra were measured using a 0.5-cm or 0.2-cm quartz cell on a JASCO V-670 spectrophotometer. CD spectra were measured using a 0.5-cm or 0.2-cm quartz cell on a JASCO J-820 spectropolarimeter. X-Ray data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation. Elemental analyses were performed at the Microanalytical Laboratory, Graduated School of Science, Osaka City University.

Synthetic Procedures and Product Characterizations

Synthesis of **5**.

Copper (II) sulfate pentahydrate (55 mg, 0.22 mmol) was added to a mixture of **3** (1.41 g, 2.8 mmol), 3-azidocoumarin **4** (517 mg, 2.8 mmol) and sodium L-ascorbate (475mg, 2.8 mmol) in MeOH / THF (v/v = 5:1, 60 mL). The heterogeneous mixture was stirred overnight, and the solvent was evaporated. CH_2Cl_2 (40 mL) was added to the residue. The organic layer was washed with water (30 mL x 3), and then dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100:3 (v/v)) to afford **5** (1.77g, 92%) as a pale yellow solid: mp 120 °C; IR (KBr) ν 3448, 2975, 2931, 1745, 1731, 1685, 1610, 1466, 1415, 1365, 1250, 1170, 1039, 981, 947, 920, 861, 772, 759 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.60 (s, 1H), 8.57 (s, 1H), 7.8–7.6 (m, 2H), 7.5–7.3 (m, 2H), 4.04 (s, 2H), 3.7–3.3 (m, 12H), 3.7–3.3 (m, 12H), 1.48 (s, 9H), 1.45 (s, 9H), 1.44 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.30, 155.88, 155.55, 152.78, 142.48, 133.10, 132.90, 129.06, 125.73, 124.22, 123.20, 118.24, 116.89, 79.75, 79.61, 79.37, 54.61, 53.37, 50.15, 47.81, 47.40, 45.03, 28.88, 28.64 ppm; Anal. Calcd for $C_{35}H_{51}N_7O_8 \cdot 0.5\ H_2O$: C, 59.47; H, 7.42; N, 13.87. Found C, 59.76; H, 7.34; N, 13.88.

Synthesis of **6**·3HCl.

Hydrochloric acid (5 M, 20 mL) was added to **5** (1.80 g, 2.7 mmol), and the mixture was stirred at 90 °C for 1 h. The solvent was evaporated, and the residue was washed successively with THF, Et_2O, and hexane, and then **6**·3HCl was obtained as a white solid (1.16 g, 81%): mp 260 °C (decomp.); IR (KBr) ν 3446, 1747, 1611, 1128, 1108, 1045, 759 cm^{-1}; ^1H NMR (D_2O, 300 MHz): δ 8.53 (s, 1H), 8.39 (s, 1H), 7.8–7.6 (m, 2H), 7.5–7.3 (m, 2H), 4.00 (s, 2H), 3.4–3.2 (m, 8H), 3.12 (br, 4H), 2.95 (br, 4H) ppm; ^{13}C NMR (D_2O, 75 MHz): δ 158.25, 152.67, 142.25, 137.86, 134.08, 129.79, 126.26, 126.15, 122.45, 117.88, 116.71, 47.89, 46.41. 44.20, 42.53, 41.94 ppm; Anal. Calcd for $C_{20}H_{27}N_7O_2 \cdot 3HCl$: C, 47.39; H, 5.97; N, 19.34. Found C, 47.20; H, 5.94; N, 19.10.

Synthesis of **2**-Na^+.

A mixture of **6**·3HCl (506 mg, 1.0 mmol), 2-(chloromethyl)pyridine hydrochloride (656 mg, 4.0 mmol), Na_2CO_3 (2.12 g, 20 mmol), and NaI (375 mg, 2.5 mmol) in CH_3CN (25 mL) was refluxed for 7 h, and the solvent was then evaporated. CH_2Cl_2 was added to the residue, and the solid was filtered. The residue was purified by column chromatography (basic Al_2O_3, CH_2Cl_2/MeOH = 100:5 (v/v)) to afford **2**-Na^+·1.5H_2O (379 mg, 48%). Mp. 220 °C (decomp.); IR (KBr) ν 3434, 2822, 1731, 1609, 1594, 1472, 1436, 1095, 1044, 997, 760 cm^{-1}; ^1H NMR (CD_3CN, 300 MHz): δ 8.40 (s, 1H), 8.16 (br s, 2H), 8.12 (s, 1H), 7.8–7.5 (m, 6H), 7.5–7.3 (m, 2H), 7.3–6.9 (m, 6H), 3.6–3.2 (m, 8H), 3.2–2.2 (br, 16H) ppm; ^{13}C NMR (CD_3CN, 75 MHz): δ 159.80, 159.76, 157.11, 153.73, 150.42, 149.88, 145.34, 137.86, 137.82, 135.24, 133.90, 130.19, 126.39, 125.33, 124.67, 124.60, 124.34, 123.17, 119.08, 117.34, 59.91, 59.66, 51.23, 51,15, 50.78, 49.28 ppm; Anal. Calcd for $C_{38}H_{42}N_{10}O_2$·NaI·1.5 H_2O: C, 53.84; H, 5.35; N, 16.52. Found C, 53.85; H, 5.19; N, 16.38.

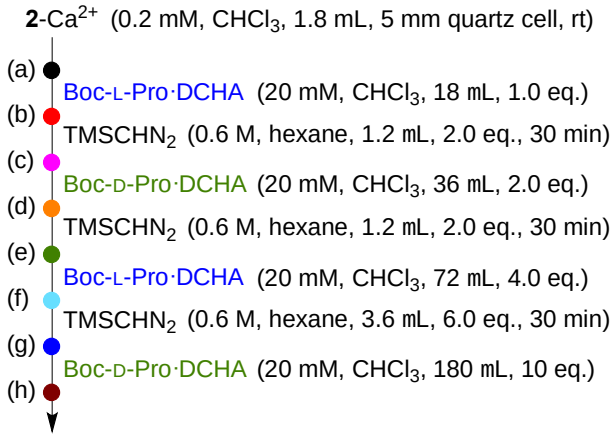
Synthesis of **2**-Ca^{2+}.

A mixture of **2**-Na^+ (121 mg, 0.15 mmol) and CaI_2 (50 mg, 0.17 mmol) in CH_3CN was stirred at 50 °C for 2 h, and the resulting solution was evaporated. CH_2Cl_2 was added to the residue, and the solid was filtered. Reprecipitation from CH_2Cl_2/hexane yielded **2**-Ca^{2+} (76.5 mg, 54 %) as a pale yellow powder. Mp. 220–30 °C (decomp.); IR (KBr) ν 3445, 2851, 1732, 1603, 1478, 1458, 1438, 1308, 1085, 1064, 1004, 958, 764 cm^{-1}; ^1H NMR (CD_3CN, 300 MHz): δ 8.50 (s, 1H), 8.13 (s, 1H), 8.0–7.7 (m, 6H), 7.5–7.3 (m, 6H), 7.3–7.1 (m, 4H), 4.1–3.4 (m, 12H), 3.2–2.8 (m, 4H), 2.6–2.3 (m, 8H) ppm; ^{13}C NMR (CD_3CN, 75 MHz): δ 159.13, 159.00, 158.84, 156.90, 154.04, 149.89, 149.12, 148.62, 145.70, 140.71, 140.65, 139.81, 137.06, 134.52, 130.50, 126.66, 126.53, 126.10, 126.04, 125.40, 125.34, 125.30, 124.46, 123.94, 118.71, 117.49, 59.56, 59.49, 59.44, 52.49, 52.43, 52.20, 52.04, 50.77, 50.69, 50.33, 49.46 ppm; Anal. Calcd for $C_{38}H_{42}N_{10}O_2$·CaI_2·2.5H_2O: C, 45.20; H, 4.69; N, 13.87. Found C, 45.05; H, 4.42; N, 13.48.

The **2**-Ca^{2+} complex for crystal structure determination was obtained by further recrystallization from CH_2Cl_2/hexane.

Chirality writing, deleting and rewriting cycle (Fig. 4)

Boc-L-Pro·DCHA (20 mM in $CHCl_3$, 18 μL) was added to the solution of **2**-Ca^{2+} (0.2 mM in $CHCl_3$, 1.8 mL, 5 mm-quarts cell). Then, $TMSCHN_2$ (0.6 M in hexane, 1.2 μL) was added to the mixture, and the resultant mixture was stirred for 30 min. In the same manner, Boc-D-Pro·DCHA (20 mM in $CHCl_3$, 36 μL), $TMSCHN_2$ (0.6 mM in hexane, 1.2 μL), Boc-L-Pro·DCHA (20 mM in $CHCl_3$, 72 μL), $TMSCHN_2$ (0.6 mM in hexane, 3.6 μL), Boc-D-Pro·DCHA (20 mM in $CHCl_3$, 180 μL) were successively added to the mixture. CD spectra were recorded on each step.



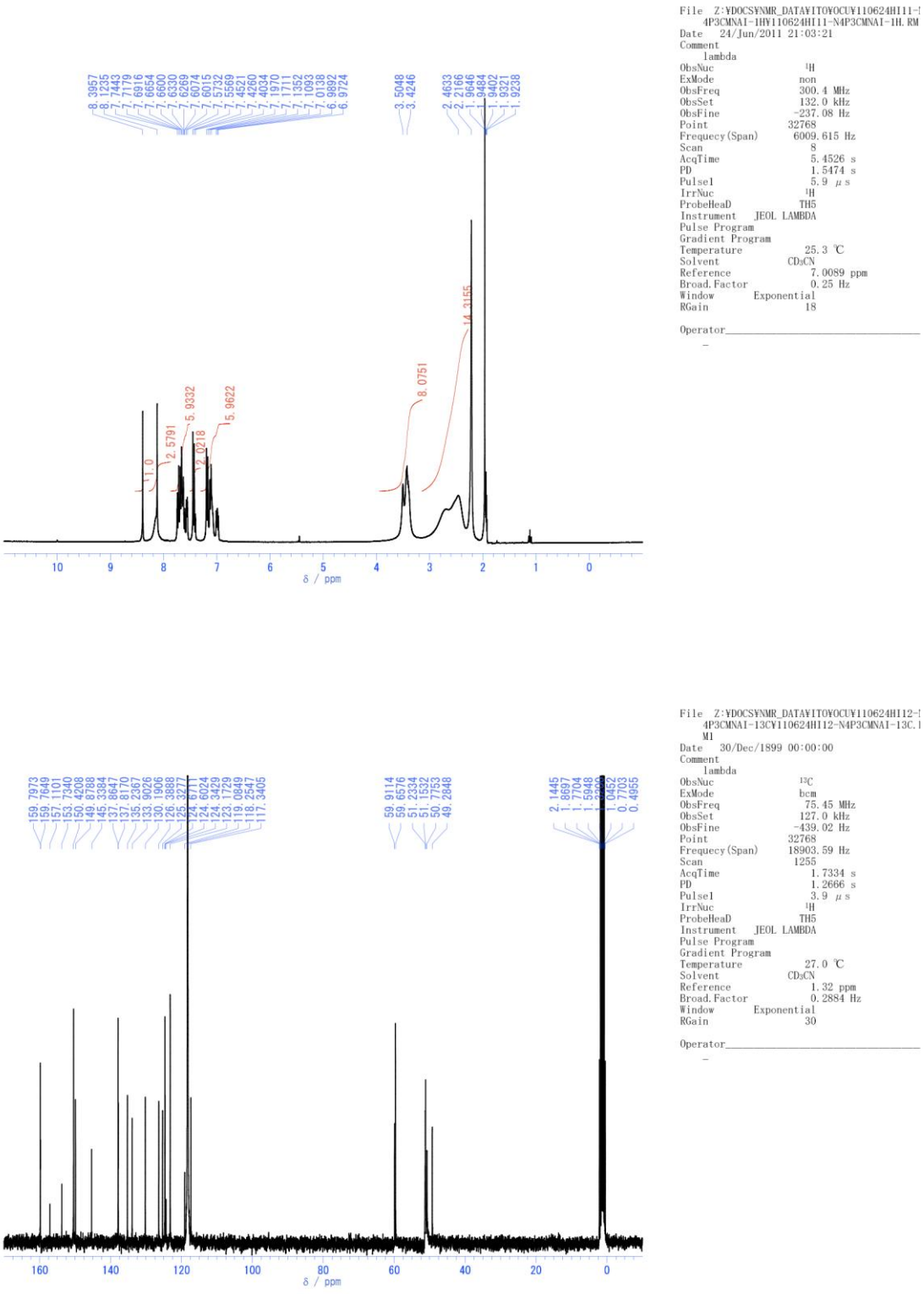


Fig. S1 ^{1}H and ^{13}C NMR spectra of **2**-Na^{+} in CD_3CN.

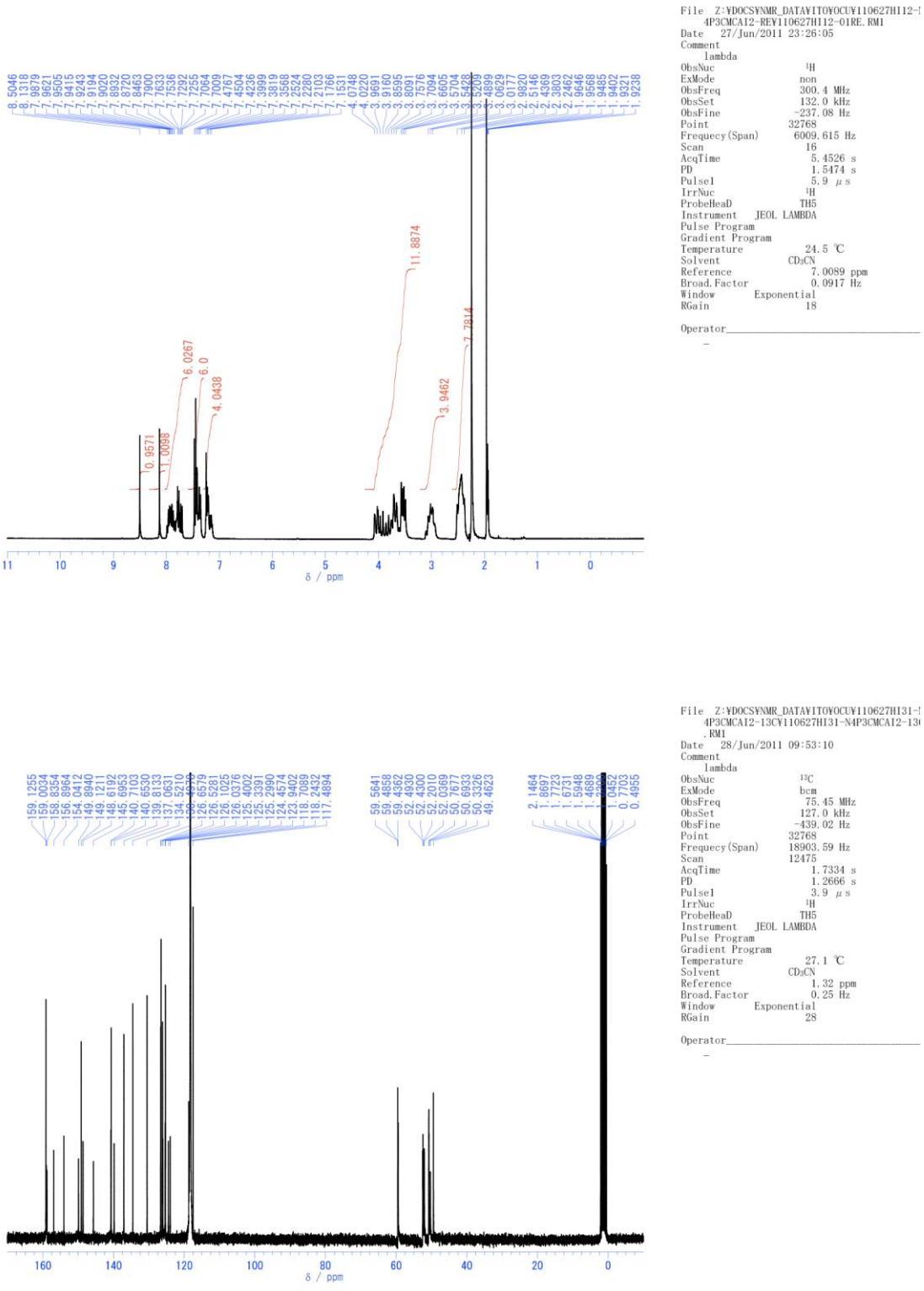


Fig. S2 ^{1}H and ^{13}C NMR spectra of **2**-Ca^{2+} in CD_3CN.

Table S1 Crystal and structure refinement data for **2**-Ca^{2+} complex.

	2-Ca^{2+}
Empirical formula	$(C_{38}H_{42}I_2N_{10}CaO_2)\cdot(CH_2Cl_2)_2\cdot 2H_2O$
Formula weight	1170.58
Crystal system, space group	Monoclinic
a / Å	11.6703(10)
b / Å	21.1654(18)
c / Å	39.374(4)
α / deg.	90
β / deg.	94.024(2)
γ / deg.	90
Volume / $Å^3$	9701.7(15)
Z	8
Calculated density / Mg m^{-3}	1.603
μ / mm^{-1}	1.672
refins collected / unique	36848 / 10392
data / restraints / params	14474 / 0 / 1135
final R indices	R1 = 0.0521
[I > 2q(I)]	wR2 = 0.1196
R indices (all data)	R1 = 0.0755
	wR2 = 0.1303
GOF	1.022

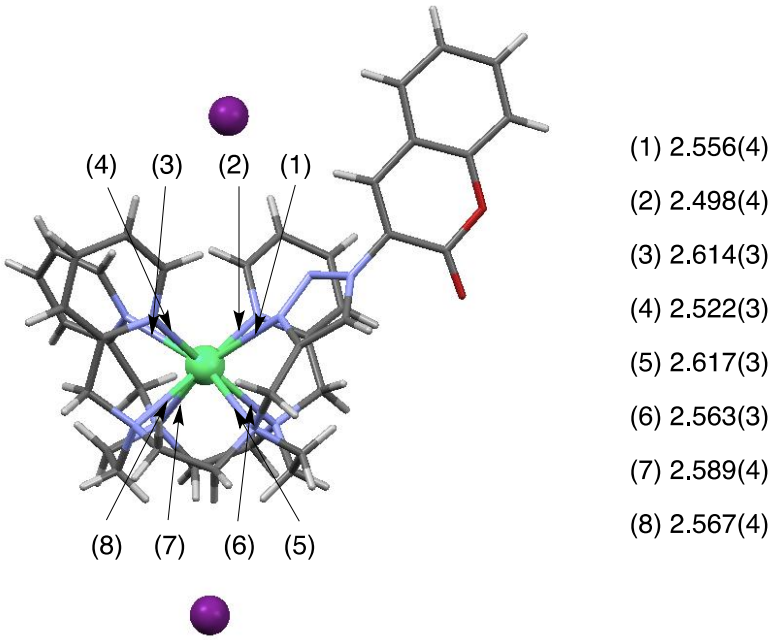


Fig. S3 Crystal structure and coordination bond lengths of **2**-Ca^{2+}.

References

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[3] F. Favarger, C. Goujon-Ginglinger, D. Monchaud, J. Lacour, *J. Org. Chem.* **2004**, *69*, 8521–8524.