Supporting Information for:

# Synthesis and optical resolution of a Cu(I) double-stranded helicate with ketimine-bridged tris(bipyridine) ligands†

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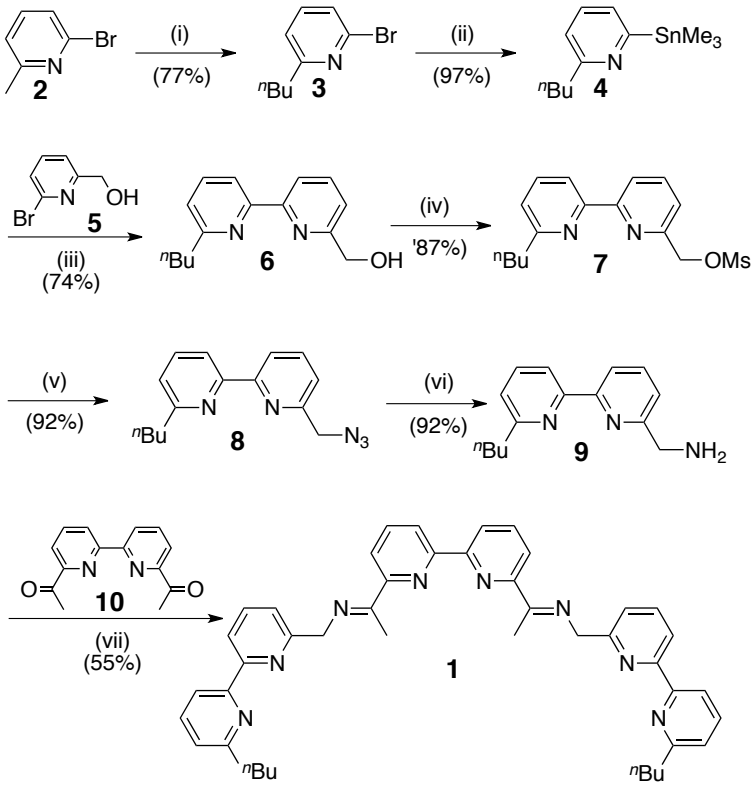
## 1. Instruments

The melting points were measured using a Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The NMR spectra were obtained using a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for $^{1}H$ and 125 MHz for $^{13}C$ using tetramethylsilane (TMS) or the solvent residual peaks as the internal standards. The electron and cold spray ionization mass spectra (ESI- and CSI-MS) were recorded on a JEOL JMS-T100CS spectrometer (Akishima, Japan). The elemental analyses were performed by the Analytical Laboratory in the Graduate School of Bioagricultural Sciences, Nagoya University. The IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The absorption and CD spectra were measured in a 0.1-, 1-, or 10-mm quartz cell on a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The temperature was controlled by a JASCO PTC-423L apparatus (25 to 70 °C). Optical rotations were taken using a JASCO P-1030 polarimeter in a 5-cm quartz cell equipped with a temperature controller (EYELA NCB-2100) (Tokyo, Japan). The single-crystal X-ray data for the helicate $[\mathbf{1}_2Cu_4](PF_6)_4$ were collected on a Bruker Smart Apex CCD-based X-ray diffractometer with Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å).

## 2. Materials

All starting materials and dehydrated solvents were purchased from Sigma-Aldrich (St. Louis, Missouri, USA), Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and Tokyo Chemical Industry Co., Ltd. (TCI) (Tokyo, Japan). Triethylamine was distilled over $CaH_2$ after being stirred with KOH pellets overnight under Ar. The deuterium solvents purchased from Merck (Darmstadt, Germany) or Cambridge Isotope Laboratories (Andover, Massachusetts, USA), were degassed with Ar and used throughout all the experiments. Silica gel ($SiO_2$) and aminopropyl-modified silica gel ($NH_2$-$SiO_2$) for the flash chromatography were purchased from Merck and Fuji Silysia Chemical Ltd. (Kasugai, Japan), respectively.

## 3. Synthesis and optical resolution of the helicates.




**Scheme S1.** Synthesis of the imine-bridged tris(bipyridine) ligand (**1**). Reagents and conditions: (i) LDA, n-PrI, THF, –78 °C to r.t.; (ii) n-BuLi, $Me_3SnCl$, THF, –78 °C to r.t.; (iii) $Pd(PPh_3)_4$, toluene, reflux; (iv) MsCl ($CH_3SO_2Cl$), $Et_3N$, THF, 0 °C; (v) $NaN_3$, DMSO, r.t.; (vi) $H_2$ (1 atm), Pd/C, MeOH, r.t.; (vii) p-toluenesulfonic acid, $C_6H_6$, reflux.

**Synthesis of 2-bromo-6-*n*-butylpyridine (3):** To a dehydrated THF (160 mL) solution of 2-bromo-6-methylpyridine (**2**) (4.84 g, 28.1 mmol) at –78 °C under nitrogen, a 1.8 M solution of lithium diisopropylamide in *n*-heptane/THF/ethylbenzene (17.0 mL, 30.6 mmol) was added dropwise within 30 min and the mixture was stirred at that temperature. After 30 min, 1-iodopropane (4.7 mL, 41.6 mmol) was added dropwise to the reaction mixture, and the mixture was allowed to warm up to room temperature. After being stirred for further 1.5 h at that temperature, the reaction was quenched with saturated aqueous $NH_4Cl$ (20 mL), and the most of the solvent was evaporated. The mixture was poured into water (100 mL) and extracted with ethyl acetate. The extract was washed with saturated aqueous $NaHCO_3$, water, and brine and dried over anhydrous $MgSO_4$. After evaporation, the residual oil was chromatographed on $SiO_2$ with *n*-hexane/ethyl acetate (20/1, v/v) as the eluent to obtain **3** as a colorless oil (4.63 g, 21.6 mmol, 77.0% yield). $^1$H NMR ($CDCl_3$): $\delta$ 0.93 (t, $J$ = 7.3 Hz, $CH_3$,

3H), 1.34–1.41 (m, C*H*$_2$CH$_3$, 2H), 1.66–1.72 (m, C*H*$_2$CH$_2$CH$_3$, 2H), 2.76 (t, *J* = 7.7 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$, 2H), 7.09 (d, *J* = 7.7 Hz, Ar-H$_5$, 1H), 7.29 (d, *J* = 7.7 Hz, Ar-H$_3$, 1H), 7.44 (t, *J* = 7.7 Hz, Ar-H$_4$, 1H). $^{13}$C NMR (CDCl$_3$): $\delta$ 13.88, 22.40, 31.89, 37.77, 121.41, 125.12, 138.52, 141.47, 164.28.

**Synthesis of 6-*n*-butyl-2-trimethylstannylpyridine (4):** To a mixture of dehydrated THF (15 mL) and a 1.6 M *n*-hexane solution of *n*-butyllithium (3.3 mL, 5.28 mmol) at –78 °C under nitrogen, a solution of **3** (1.10 g, 5.15 mmol) in dehydrated THF (10 mL) was added dropwise within 30 min, and the mixture was stirred at that temperature. After 30 min, a 1.0 M solution of trimethyltin chloride in THF (5.6 mL, 5.6 mmol) was added dropwise over a period of 15 min, and the mixture was allowed to warm up to room temperature. After being stirred for further 10 h at that temperature, the solvent was evaporated. The residual oil was rinsed with diethyl ether, and the solid (LiCl) was then removed by filtration. The ethereal solution was concentrated under reduced pressure to obtain **4** as a pale yellow oil (1.53 g, 5.13 mmol, 97.2% yield) that was used in the next step without further purification. $^1$H NMR (CDCl$_3$): $\delta$ 0.32 (s, SnCH$_3$, 9H), 0.94 (t, *J* = 7.4 Hz, CH$_3$, 3H), 1.35–1.44 (m, C*H*$_2$CH$_3$, 2H), 1.67–1.75 (m, CH$_2$C*H*$_2$CH$_3$, 2H), 2.78 (t, *J* = 7.7 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$, 2H), 6.97 (d, *J* = 7.7 Hz, Ar-H$_5$, 1H), 7.23 (d, *J* = 7.7 Hz, Ar-H$_3$, 1H), 7.40 (t, *J* = 7.7 Hz, Ar-H$_4$, 1H). $^{13}$C NMR (CDCl$_3$): $\delta$ –9.35, 14.00, 22.50, 32.03, 38.34, 121.13, 128.75, 133.53, 162.74, 172.42.

**Synthesis of 6'-*n*-butyl-6-hydroxymethyl-2,2'-bipyridine (6):** To a dehydrated toluene (70 mL) solution of **4** (1.32 g, 4.43 mmol) and **5**[1] (1.08 g, 5.74 mmol), tetrakis(triphenylphosphine)palladium(0) (597 mg, 0.517 mmol) was added under nitrogen, and the mixture was refluxed for 10 h. The mixture was poured into saturated aqueous NH$_4$Cl (100 mL) and extracted with ethyl acetate. The extract was washed with water and brine and dried over anhydrous MgSO$_4$. After evaporation, the residual oil was chromatographed on NH$_2$-SiO$_2$ with CHCl$_3$/ethyl acetate (1/1, v/v) as the eluent to obtain **6** as a white solid (791 mg, 3.26 mmol, 73.7% yield). $^1$H NMR (CDCl$_3$): $\delta$ 0.97 (t, *J* = 7.4 Hz, CH$_3$, 3H), 1.39–1.47 (m, C*H*$_2$CH$_3$, 2H), 1.76–1.83 (m, C*H*$_2$CH$_2$CH$_3$, 2H), 2.87 (t, *J* = 7.7 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$, 2H), 4.10 (t, *J* = 5.0 Hz, OH, 1H), 4.82 (d, *J* = 5.0 Hz, CH$_2$O, 2H), 7.17 (d, *J* = 7.7 Hz, Ar-H$_{5'}$, 1H), 7.21 (d, *J* = 7.7 Hz, Ar-H$_5$, 1H), 7.72 (t, *J* = 7.7 Hz, Ar-H$_{4'}$, 1H), 7.81 (t, *J* = 7.7 Hz, Ar-H$_4$, 1H), 8.21 (d, *J* = 7.7 Hz, Ar-H$_{3'}$, 1H), 8.38 (d, *J* = 7.7 Hz, Ar-H$_3$, 1H). $^{13}$C NMR

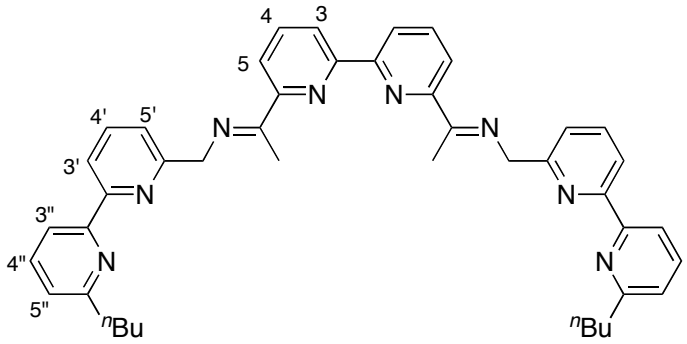
($CDCl_3$): $\delta$ 14.00, 22.47, 31.84, 38.10, 63.82, 118.05, 119.80, 120.09, 122.85, 136.94, 137.54, 154.86, 155.31, 157.84, 162.04.

**Synthesis of 6'-*n*-butyl-6-methanesulfonyloxymethyl-2,2'-bipyridine (7):** To a dehydrated THF (30 mL) solution of **6** (105 mg, 0.433 mmol) at 0 °C under nitrogen, triethylamine (120 $\mu$L, 0.859 mmol) and methanesulfonyl chloride (60 $\mu$L, 0.614 mmol) were added dropwise, and the mixture was stirred at room temperature. After 10 h, the mixture was quenched with saturated aqueous $NH_4Cl$ (20 mL), and the most of the solvent was evaporated. The mixture was poured into water (100 mL) and extracted with ethyl acetate. The extract was washed with brine and dried over anhydrous $MgSO_4$. After evaporation, the residual oil was chromatographed on $NH_2$-$SiO_2$ with *n*-hexane/ethyl acetate (1/1, v/v) to obtain **7** as a white solid (121 mg, 0.378 mmol, 87.2% yield). $^1$H NMR ($CDCl_3$): $\delta$ 0.97 (t, $J$ = 7.4 Hz, $CH_3$, 3H), 1.39–1.47 (m, C*H*$_2$CH$_3$, 2H), 1.76–1.83 (m, C*H*$_2$CH$_2$CH$_3$, 2H), 2.86 (t, $J$ = 7.7 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$, 2H), 3.09 (s, $CH_3$, 3H), 5.41 (s, $CH_2O$, 2H), 7.18 (d, $J$ = 7.7 Hz, Ar-H$_{5'}$, 1H), 7.46 (d, $J$ = 7.7 Hz, Ar-H$_5$, 1H), 7.71 (t, $J$ = 7.7 Hz, Ar-H$_{4'}$, 1H), 7.87 (t, $J$ = 7.7 Hz, Ar-H$_4$, 1H), 8.19 (d, $J$ = 7.7 Hz, Ar-H$_{3'}$, 1H), 8.46 (d, $J$ = 7.7 Hz, Ar-H$_3$, 1H). $^{13}$C NMR ($CDCl_3$): $\delta$ 13.98, 22.45, 31.82, 38.06, 38.19, 71.99, 118.19, 121.07, 122.09, 123.01, 137.01, 137.89, 152.80, 154.72, 156.62, 162.07.

**Synthesis of 6-azidomethyl-6'-*n*-butyl-2,2'-bipyridine (8):** To a DMSO (30 mL) solution of **7** (929 mg, 2.90 mmol), sodium azide (401 mg, 6.16 mmol) was added at room temperature. After being stirred for 3 h, the mixture was poured into water (100 mL) and extracted with $Et_2O$. The extract was washed with brine and dried over anhydrous $MgSO_4$. After evaporation, the residual oil was chromatographed on $NH_2$-$SiO_2$ with *n*-hexane/ethyl acetate (3/1, v/v) to obtain **8** as a white solid (715 mg, 2.67 mmol, 92.2% yield). $^1$H NMR ($CDCl_3$): $\delta$ 0.97 (t, $J$ = 7.4 Hz, $CH_3$, 3H), 1.39–1.47 (m, C*H*$_2$CH$_3$, 2H), 1.76–1.83 (m, C*H*$_2$CH$_2$CH$_3$, 2H), 2.86 (t, $J$ = 7.7 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$, 2H), 4.50 (s, $CH_2N_3$, 2H), 7.16 (d, $J$ = 7.7 Hz, Ar-H$_{5'}$, 1H), 7.30 (d, $J$ = 7.7 Hz, Ar-H$_5$, 1H), 7.72 (t, $J$ = 7.7 Hz, Ar-H$_{4'}$, 1H), 7.83 (t, $J$ = 7.7 Hz, Ar-H$_4$, 1H), 8.24 (d, $J$ = 7.7 Hz, Ar-H$_{3'}$, 1H), 8.42 (d, $J$ = 7.7 Hz, Ar-H$_3$, 1H). $^{13}$C NMR ($CDCl_3$): $\delta$ 14.00, 22.47, 31.86, 38.09, 55.40, 118.39, 120.31, 121.55, 122.87, 137.05, 137.78, 155.02, 155.10, 156.66, 161.92.

**6-Aminomethyl-6'-*n*-butyl-2,2'-bipyridine (9):** A $CH_3OH$ (15 mL) solution of **8** (676 mg, 2.53 mmol) was stirred in the presence of 10% Pd/C (21.6 mg) under a hydrogen atmosphere (balloon) at room temperature for 1 day. After Pd catalyst was removed by filtration and the filtrate was concentrated, the residual oil was chromatographed on $NH_2$-$SiO_2$ with $CHCl_3$/$CH_3OH$ (100/1, v/v) to obtain **9** as a white solid (559 mg, 2.32 mmol, 91.6% yield). $^1$H NMR ($CDCl_3$): $\delta$ 0.97 (t, $J$ = 7.4 Hz, $CH_3$, 3H), 1.39–1.47 (m, C*H*$_2$CH$_3$, 2H), 1.76–1.83 (m, C*H*$_2$CH$_2$CH$_3$, 2H), 2.86 (t, $J$ = 7.7 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$, 2H), 4.03 (s, $CH_2N$, 2H), 7.15 (d, $J$ = 7.7 Hz, Ar-H$_{5'}$, 1H), 7.24 (d, $J$ = 7.7 Hz, Ar-H$_5$, 1H), 7.70 (t, $J$ = 7.7 Hz, Ar-H$_{4'}$, 1H), 7.76 (t, $J$ = 7.7 Hz, Ar-H$_4$, 1H), 8.25 (d, $J$ = 7.7 Hz, Ar-H$_{3'}$, 1H), 8.31 (d, $J$ = 7.7 Hz, Ar-H$_3$, 1H). $^{13}$C NMR ($CDCl_3$): $\delta$ 13.99, 22.46, 31.86, 38.11, 47.78, 118.14, 119.20, 120.91, 122.60, 136.86, 137.26, 155.55, 156.07, 161.06, 161.89.

**Synthesis of 6,6'-bis(1-(*N*-(6'-*n*-butyl-[2,2']bipyridin-6-yl)methylimino)ethyl)-2,2'-bipyridine (1):** To a dehydrated benzene (35 mL) solution of **9** (65.0 mg, 0.269 mmol) and **10**[2] (32.4 mg, 0.135 mmol), *p*-toluenesulfonic acid (PTSA) (1.5 mg, 8.7 $\mu$mol) was added, and the mixture was refluxed for 1 day equipped with a Dean-Stark trap to yield a colorless precipitate. The crude product was filtered at room temperature and washed with benzene to afford **1** as a white powder (50.9 mg, 74.2 $\mu$mol, 55.2% yield). The $^{13}$C NMR spectrum of **1** in $CD_2Cl_2$ could not be measured because of its low solubility (less than 1 mM) in nonpolar solvents. Mp: 253–256 °C. IR (KBr, cm$^{-1}$): 2957, 2925, 1702, 1633, 1574, 1437, 1384, 1071, 799. $^1$H NMR ($CD_2Cl_2$): $\delta$ 0.98 (t, $J$ = 7.4 Hz, $CH_3$, 6H), 1.40–1.48 (m, C*H*$_2$CH$_3$, 4H), 1.76–1.83 (m, C*H*$_2$CH$_2$CH$_3$, 4H), 2.68 (s, $CH_3$C=N), 6H), 2.86 (t, $J$ = 7.7 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$, 4H), 5.00 (s, $CH_2$N=C), 4H), 7.18 (d, $J$ = 7.7 Hz, Ar-H$_{5''}$, 2H), 7.69 (d, $J$ = 7.7 Hz, Ar-H$_{5'}$, 2H), 7.72 (t, $J$ = 7.7 Hz, Ar-H$_{4''}$, 2H), 7.86 (t, $J$ = 7.7 Hz, Ar-H$_{4'}$, 2H), 7.93 (t, $J$ = 7.7 Hz, Ar-H$_4$, 2H), 8.26 (d, $J$ = 7.7 Hz, Ar-H$_{3''}$, 2H), 8.31 (d, $J$ = 7.7 Hz, Ar-H$_5$, 2H), 8.36 (d, $J$ = 7.7 Hz, Ar-H$_{3'}$, 2H), 8.63 (d, $J$ = 7.7 Hz, Ar-H$_3$, 2H). ESI-MS ($CH_2Cl_2$/$CH_3OH$ (1/1, v/v), positive): Calcd for $C_{44}H_{47}N_8$ [**1**+H]$^+$: $m/z$ = 687.39. Found: $m/z$ = 687.29. Elemental Anal. Calcd for $C_{44}H_{46}N_8$: C, 76.94; H, 6.75; N, 16.31. Found: C, 76.94; H, 6.59; N, 16.09.




**Synthesis of pyridinium (*R*)-(–)-1,1'-binaphthyl-2,2'-diyl phosphate ((*R*)-BNP·py):** To a suspension of (*R*)-(–)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (1.00 g, 2.87 mmol) in $CH_2Cl_2$ was added pyridine (1 mL) at room temperature, and the mixture was stirred for 30 min. After evaporation in vacuo, the crude product dissolved in a small amount of $CH_2Cl_2$ was poured into a large amount of $Et_2O$. The precipitate was collected by centrifugation, washed with $Et_2O$, and dried in vacuo to afford (*R*)-BNP·py as a white powder (1.10 g, 2.57 mmol, 89.6% yield). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.28 (m, Ar-H, 2H), 7.36 (d, $J$ = 8.0 Hz, Ar-H, 2H), 7.45 (m, Ar-H, 2H), 7.50 (dd, $J$ = 8.0, 5.0 Hz, Py-$H_{3,5}$, 2H), 7.54 (d, $J$ = 8.0 Hz, Ar-H, 2H), 7.91 (d, $J$ = 8.0 Hz, Ar-H, 2H), 7.94 (d, $J$ = 8.0 Hz, Ar-H, 2H), 8.08 (t, $J$ = 8.0 Hz, Py-$H_4$, 1H), 8.46 (d, $J$ = 5.0 Hz, Py-$H_{2,6}$, 2H).

**Synthesis of pyridinium (*S*)-(+)-1,1'-binaphthyl-2,2'-diyl phosphate ((*S*)-BNP·py):** The title compound was prepared in the same way as that for (*R*)-BNP·py using (*S*)-(+)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate. 94.1% yield. $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.28 (m, Ar-H, 2H), 7.36 (d, $J$ = 8.0 Hz, Ar-H, 2H), 7.45 (m, Ar-H, 2H), 7.50 (dd, $J$ = 8.0, 5.0 Hz, Py-$H_{3,5}$, 2H), 7.54 (d, $J$ = 8.0 Hz, Ar-H, 2H), 7.92 (d, $J$ = 8.0 Hz, Ar-H, 2H), 7.94 (d, $J$ = 8.0 Hz, Ar-H, 2H), 8.09 (t, $J$ = 8.0 Hz, Py-$H_4$, 1H), 8.46 (d, $J$ = 5.0 Hz, Py-$H_{2,6}$, 2H).

**Synthesis of (±)-[$1_2Cu_4$](OTf)$_4$:** A dehydrated $CH_3CN$ (0.5 mL) solution of copper(I) trifluoromethanesulfonate benzene complex (tech. 90%, 14.5 mg, 57.6 mmol) prepared in a dry-box under an argon atmosphere was added to **1** (9.9 mg, 14.4 mmol), and the solution color became dark brown. After concentration, the crude product dissolved in a small amount of dehydrated $CH_3CN$ (*ca*. 200 mL) was adsorbed on neutral alumina for chromatography (10 cm × $\phi$ 1 cm (i.d.)), washed with dehydrated $CH_2Cl_2$, and collected with the dehydrated $CH_2Cl_2$/$CH_3OH$ (80/20, v/v) mixture. After evaporation *in vacuo*, the crude product dissolved

in a small amount of $CH_3CN$ was poured into a large amount of dehydrated benzene, and then the precipitate was collected by centrifugation (3,000 rpm, 20 min), washed with benzene, and dried *in vacuo* to obtain the racemic $[\mathbf{1}_2Cu_4](OTf)_4$ as a dark brown solid (15.2 mg, 6.85 mmol, 95.1% yield). IR (KBr, $cm^{-1}$): 3074, 2957, 2929, 2871, 1638, 1598, 1460, 1431, 1380, 1262, 1159, 1031, 800, 638. $^1$H NMR ($CD_3CN$): $\delta$ 0.25 (t, $J$ = 7.4 Hz, $CH_3$, 12H), 0.57–0.75 (m, C*H*$_2$CH$_3$, 8H), 1.05–1.29 (m, C*H*$_2$CH$_2$CH$_3$, 8H), 1.32 (s, $CH_3$C=N, 12H), 2.05–2.34 (m, C*H*$_2$CH$_2$CH$_2$CH$_3$, 8H), 3.34 (d, $J$ = 18.2 Hz, $CH_2$N=C, 4H), 3.45 (d, $J$ = 18.2 Hz, $CH_2$N=C, 4H), 7.13 (d, $J$ = 7.8 Hz, Ar-H$_{5'}$, 4H), 7.48 (d, $J$ = 7.5 Hz, Ar-H$_{5''}$, 4H), 7.69 (t, $J$ = 7.8 Hz, Ar-H$_{4'}$, 4H), 7.72 (d, $J$ = 7.9 Hz, Ar-H$_5$, 4H), 7.77 (d, $J$ = 7.8 Hz, Ar-H$_{3'}$, 4H), 8.01–8.07 (m, Ar-H$_{3,3'',4''}$, 12H), 8.23 (t, $J$ = 7.9 Hz, Ar-H$_4$, 4H). $^{13}$C NMR ($CD_3CN$): $\delta$ 13.33, 15.50, 22.86, 31.69, 39.63, 58.04 121.10, 122.81, 125.28, 126.76, 127.61, 129.40, 139.26, 139.95, 140.35, 151.79, 151.85, 152.59, 153.79, 154.79, 162.47, 167.68. CSI-MS ($CH_2Cl_2$/$CH_3OH$ (80/20, v/v), –30 °C, 30 V, positive): Calcd for $C_{90}H_{92}Cu_4F_6N_{16}O_6S_2$ $[[\mathbf{1}_2Cu_4](OTf)_2]^{2+}$: $m/z$ = 963.20. Found: $m/z$ = 963.15.

**Synthesis of (±)-$[\mathbf{1}_2Cu_4](PF_6)_4$:** This compound was prepared in the similar way for the synthesis of $[\mathbf{1}_2Cu_4](OTf)_4$ using tetrakis(acetonitrile)copper(I) hexafluorophosphate, giving a dark brown solid of (±)-$[\mathbf{1}_2Cu_4](PF_6)_4$ in 97.8% yield. IR (KBr, $cm^{-1}$): 3107, 2957, 2931, 2873, 1637, 1598, 1465, 1422, 1380, 1302, 1259, 1175, 1103, 1011, 842, 798. $^1$H NMR ($CD_3CN$): $\delta$ 0.25 (t, $J$ = 7.4 Hz, $CH_3$, 12H), 0.56–0.75 (m, C*H*$_2$CH$_3$, 8H), 1.05–1.28 (m, C*H*$_2$CH$_2$CH$_3$, 8H), 1.31 (s, $CH_3$C=N, 12H), 2.05–2.32 (m, C*H*$_2$CH$_2$CH$_2$CH$_3$, 8H), 3.31 (d, $J$ = 18.1 Hz, $CH_2$N=C, 4H), 3.46 (d, $J$ = 18.1 Hz, $CH_2$N=C, 4H), 7.08 (d, $J$ = 7.8 Hz, Ar-H$_{5'}$, 4H), 7.48 (d, $J$ = 7.5 Hz, Ar-H$_{5''}$, 4H), 7.66 (t, $J$ = 7.8 Hz, Ar-H$_{4'}$, 4H), 7.69 (d, $J$ = 7.9 Hz, Ar-H$_5$, 4H), 7.74 (d, $J$ = 7.8 Hz, Ar-H$_{3'}$, 4H), 7.95 (d, $J$ = 7.9 Hz, Ar-H$_3$, 4H), 8.00 (d, $J$ = 7.5 Hz, Ar-H$_{3''}$, 4H), 8.04 (t, $J$ = 7.5 Hz, Ar-H$_{4''}$, 4H), 8.20 (t, $J$ = 7.9 Hz, Ar-H$_4$, 4H). $^{13}$C NMR ($CD_3CN$): $\delta$ 13.33, 15.37, 22.86, 31.69, 39.62, 58.03 121.02, 122.77, 125.23, 126.81, 127.46, 129.17, 139.15, 139.96, 140.27, 151.73, 151.90, 152.64, 153.77, 154.77, 162.52, 167.69. CSI-MS ($CH_2Cl_2$/$CH_3OH$ (80/20, v/v), –30 °C, 80 V, positive): Calcd for $C_{88}H_{92}Cu_4F_{12}N_{16}P_2$ $[[\mathbf{1}_2Cu_4](PF_6)_2]^{2+}$: $m/z$ = 958.21. Found: $m/z$ = 958.10.

**Single crystal X-ray analysis of $[\mathbf{1}_2Cu_4](PF_6)_4$:** Single crystals of $[\mathbf{1}_2Cu_4](PF_6)_4$ $[[C_{88}H_{92}N_{16}Cu_4]\cdot(PF_6)_4\cdot(H_2O)$, Mw = 2225.86] suitable for X-ray analysis were grown by

slow evaporation of a toluene solution the complex, and a single colorless crystal with dimensions of 0.60 × 0.03 × 0.01 $mm^3$ was selected for intensity measurements. The unit cell was monoclinic with the space group *P2/c*. The lattice constants with $Z = 4$, $\rho_{calcd} = 1.635$ g $cm^{-3}$, $\mu$(Mo-K) = 1.106 $cm^{-1}$, $F(000) = 4528$, $2\theta_{max} = 46.5^o$ were $a = 32.027(9)$ Å, $b = 11.894(3)$, $c = 24.907(7)$ Å, $\beta = 107.539(3)^o$, and $V = 9047(4)$ $Å^3$. A total of 35152 reflections were collected, of which 12956 reflections were independent ($R_{int} = 0.0972$). The structure was refined to final $R_1 = 0.1338$ for 12956 data [$I>2\sigma(I)$] with 1235 parameters and $wR_2 = 0.3032$ for all data, $GOF = 1.168$, and residual electron density max./min. = 1.302/ –2.109 $e^{\cdot}Å^{-3}$.

The structure was solved by direct methods using SHELXS-97[3] and refined by full-matrix least squares methods on $F^2$ using SHELXL-97.[3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated geometrically and refined as the riding models. The water hydrogen atoms were not located because they have disordered configurations.

CCDC 818166 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Optical resolution of the helicate:** A dehydrated $CH_3CN$ (0.5 mL) solution of copper(I) trifluoromethanesulfonate benzene complex (tech. 90%, 14.5 mg, 57.6 mmol) prepared in a dry-box under an argon atmosphere was added to **1** (9.9 mg, 14.4 mmol) under argon, and the solution color became dark brown. After concentration, the crude product dissolved in a small amount of dehydrated $CH_3CN$ (ca. 200 mL) was adsorbed on neutral alumina for chromatography (10 cm × $\phi$ 1 cm (i.d.)), washed with dehydrated $CH_2Cl_2$, and collected with the dehydrated $CH_2Cl_2/CH_3OH$ (80/20, v/v) mixture. After evaporation in vacuo, the crude product and (*S*)-BNP·py (50 mg, 117 mmol) were dissolved in a small amount of dehydrated $CH_2Cl_2$ and the mixture was poured into a large amount of dehydrated benzene. The precipitate was collected by centrifugation (10,000 rpm, 15 min) and subsequent decantation. The same operations from the addition of (*S*)-BNP·py to the removal of the supernatant were repeatedly done further two times. After washed with dehydrated benzene, the crude product was crystallized using the solvent diffusion method with dehydrated $CH_2Cl_2/CH_3OH$ (1/1, v/v) (1 mL) and benzene (3 mL). After 2 days, the crystallized black powder was collected by

centrifugation (6,000 rpm, 15 min), washed with dehydrated benzene, and dried in vacuo to obtain the diastereomer $(-)_{310}$-[**1**$_2$Cu$_4$]((*S*)-BNP·py)$_4$ as a dark brown solid (3.8 mg, 1.26 mmol, 17.5% yield). $^1$H NMR ($CD_2Cl_2$/$CD_3OD$ (80/20, v/v): $\delta$ 0.27 (t, $J$ = 7.4 Hz, $CH_3$, 12H), 0.57–0.73 (m, C$H_2$CH$_3$, 8H), 1.03–1.24 (m, C$H_2$CH$_2$CH$_3$, 8H), 1.32 (s, CH$_3$C=N, 12H), 2.03–2.22 (m, C$H_2$CH$_2$CH$_2$CH$_3$, 8H), 3.32–3.38 (br, CH$_2$N=N, 8H), 7.13 (br, Ar-H, 4H), 7.24 (t, $J$ = 7.4 Hz, Ar-H, 8H), 7.43 (d, $J$ = 7.8 Hz, Ar-H, 8H), 7.37 (d, $J$ = 6.4 Hz, Ar-H, 4H), 7.43 (t, $J$ = 7.1 Hz, Ar-H, 8H), 7.51–7.67 (br, Ar-H, 8H), 7.63 (br, Ar-H, 8H), 7.72 (d, $J$ = 7.5 Hz, Ar-H, 4H), 7.95 (d, $J$ = 8.1 Hz, Ar-H, 8H), 7.98 (d, $J$ = 6.6 Hz, Ar-H, 8H), 8.05 (br, Ar-H, 8H), 8.17 (t, $J$ = 7.4 Hz, Ar-H, 4H), 8.31 (t, $J$ = 7.0 Hz, Ar-H, 4H). CSI-MS ($CH_2Cl_2$/$CH_3OH$ (95/5, v/v), –30 °C, 30 V, positive): Calcd for $C_{128}H_{116}Cu_4N_{16}O_8P_2$ [[**1**$_2$Cu$_4$]((*S*)-BNP)$_2$]$^{2+}$: $m/z$ = 1161.29. Found: $m/z$ = 1161.24.

After the addition of $NH_4PF_6$ (20 mg, 123 mmol) to the diastereomer, the $CH_3CN$-soluble fraction was collected by membrane filtration. After evaporation in vacuo, the sample dissolved in a small amount of dehydrated $CH_3CN$ was poured into a large amount of dehydrated ethyl acetate. The precipitate was collected by centrifugation (10,000 rpm, 15 min), washed with ethyl acetate and benzene, and dried in vacuo to obtain the enantiomer $(-)_{310}$-[**1**$_2$Cu$_4$](PF$_6$)$_4$ as a dark brown solid (2.3 mg, 1.04 mmol, 82.5% yield). $^1$H NMR ($CD_2Cl_2$/$CD_3OD$ (80/20, v/v): $\delta$ 0.27 (t, $J$ = 7.4 Hz, $CH_3$, 12H), 0.58–0.75 (m, C$H_2$CH$_3$, 8H), 1.05–1.27 (m, C$H_2$CH$_2$CH$_3$, 8H), 1.32 (s, CH$_3$C=N, 12H), 2.05–2.29 (m, C$H_2$CH$_2$CH$_2$CH$_3$, 8H), 3.33 (d, $J$ = 18.3 Hz, CH$_2$N=C, 4H), 3.44 (d, $J$ = 18.3 Hz, CH$_2$N=C, 4H), 7.07 (d, $J$ = 7.8 Hz, Ar-H$_{5'}$, 4H), 7.42 (d, $J$ = 7.5 Hz, Ar-H$_{5''}$, 4H), 7.67 (t, $J$ = 7.8 Hz, Ar-H$_{4'}$, 4H), 7.69 (d, $J$ = 7.9 Hz, Ar-H$_5$, 4H), 7.70 (d, $J$ = 7.8 Hz, Ar-H$_{3'}$, 4H), 7.95 (d, $J$ = 7.9 Hz, Ar-H$_3$, 4H), 7.98 (d, $J$ = 7.5 Hz, Ar-H$_{3''}$, 4H), 8.01 (t, $J$ = 7.5 Hz, Ar-H$_{4''}$, 4H), 8.26 (t, $J$ = 7.9 Hz, Ar-H$_4$, 4H). CSI-MS ($CH_2Cl_2$/$CH_3OH$ (80/20, v/v), –30 °C, 80 V, positive): Calcd for $C_{88}H_{92}Cu_4F_{12}N_{16}P_2$ [[**1**$_2$Cu$_4$](PF$_6$)$_2$]$^{2+}$: $m/z$ = 958.21. Found: $m/z$ = 958.10.

$(+)_{310}$-[**1**$_2$Cu$_4$]((*R*)-BNP·py)$_4$ and $(+)_{310}$-[**1**$_2$Cu$_4$](PF$_6$)$_4$ were also obtained according to the same procedure using (*R*)-BNP·Py.

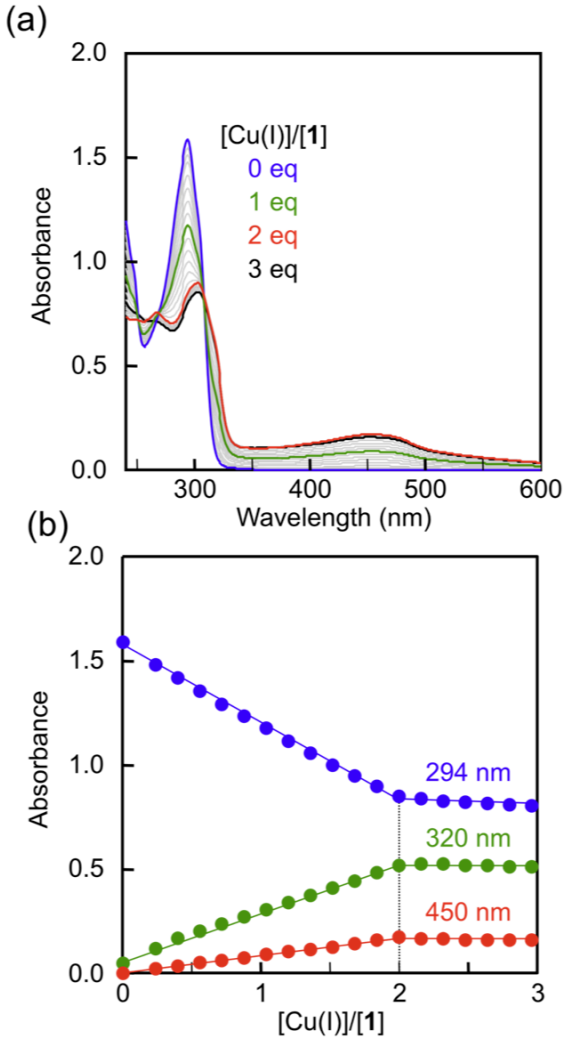



**Fig. S1.** (a) Absorption titration of **1** in $CH_2Cl_2$ (29.1 mM, 2 mL) with increasing amounts of $[Cu(CH_3CN)_4]PF_6$ in $CH_2Cl_2/CH_3CN$ (1/1, v/v) (0.467 mM, 0–250 mL) at 25 °C. (b) Plots of the absorbance changes at 294, 320, and 450 nm.

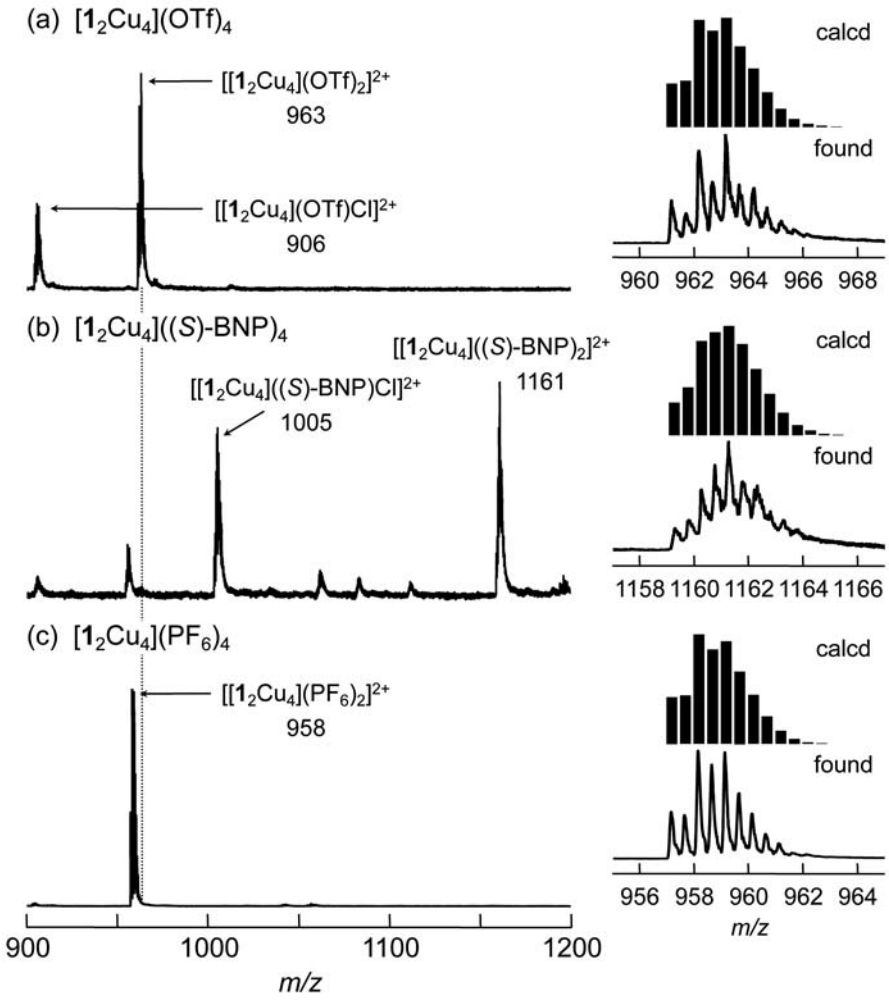



**Fig. S2.** CSI-MS spectra of (a) (±)-[**1**$_2$Cu$_4$](OTf)$_4$ ($CH_2Cl_2$/$CH_3OH$ = 95/5 (v/v), orifice 1 voltage = 30 V), (b) (–)$_{310}$-[**1**$_2$Cu$_4$]((S)-BNP)$_4$ obtained by crystallization of (±)-[**1**$_2$Cu$_4$]((S)-BNP)$_4$ from $CH_3CN$ ($CH_2Cl_2$/$CH_3OH$ = 95/5 (v/v), orifice 1 voltage = 30 V), and (c) (–)$_{310}$-[**1**$_2$Cu$_4$](PF$_6$)$_4$ obtained by the anion exchange of (–)$_{310}$-[**1**$_2$Cu$_4$]((S)-BNP)$_4$ with $NH_4PF_6$ ($CH_2Cl_2$/$CH_3OH$ = 80/20 (v/v,) orifice 1 voltage = 80 V) at –30 °C.

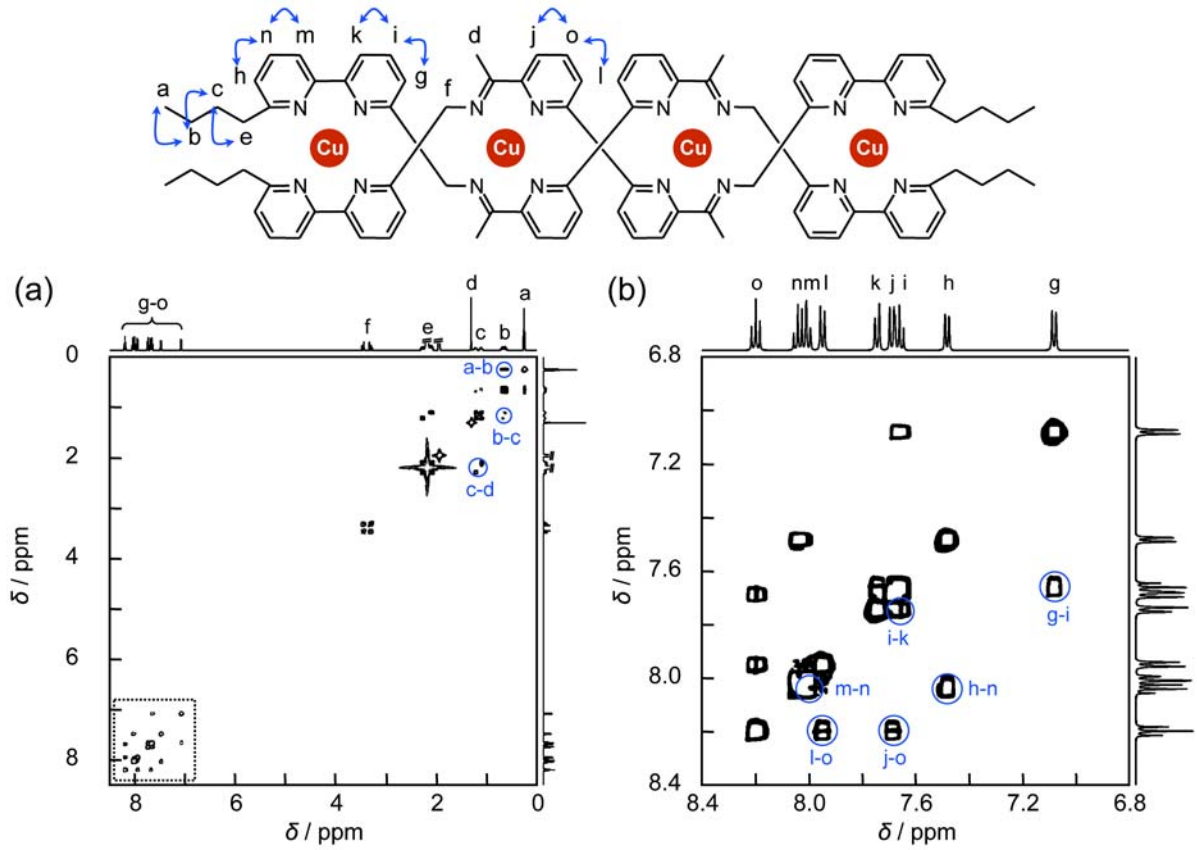



**Fig. S3.** Full (a) and partial (b) gCOSY spectra (500 MHz, $CD_3CN$, 0.5 mM, 25 °C) of $[\mathbf{1}_2Cu_4](PF_6)_4$.

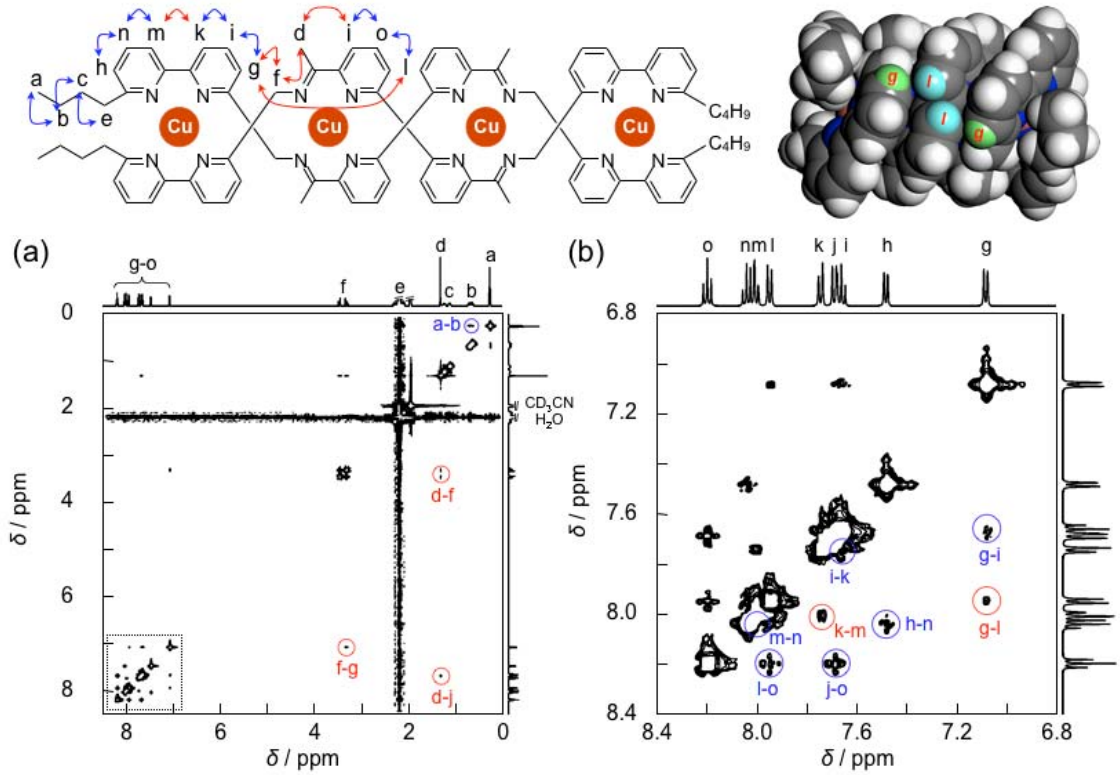



**Fig. S4.** Full (a) and partial (b) NOESY spectra (500 MHz, $CD_3CN$, 0.5 mM, 25 °C, mixing time = 0.3 s) of $[\mathbf{1}_2Cu_4](PF_6)_4$.

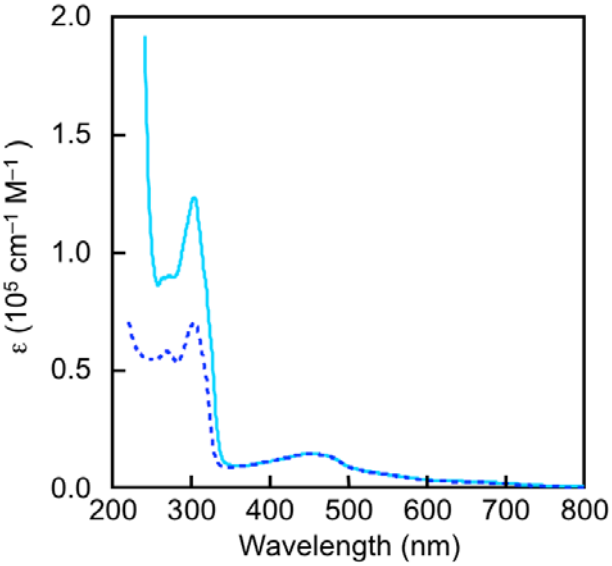



**Fig. S5.** Absorption spectra of $(+)_{310}$-$[\mathbf{1}_2Cu_4]$((R)-BNP)$_4$ (aqua) in $CD_2Cl_2/CD_3CN$ (80/20, v/v) and $(+)_{310}$-$[\mathbf{1}_2Cu_4](PF_6)_4$ (blue) in $CD_2Cl_2/CD_3CN$ (90/10, v/v) at 25 °C.

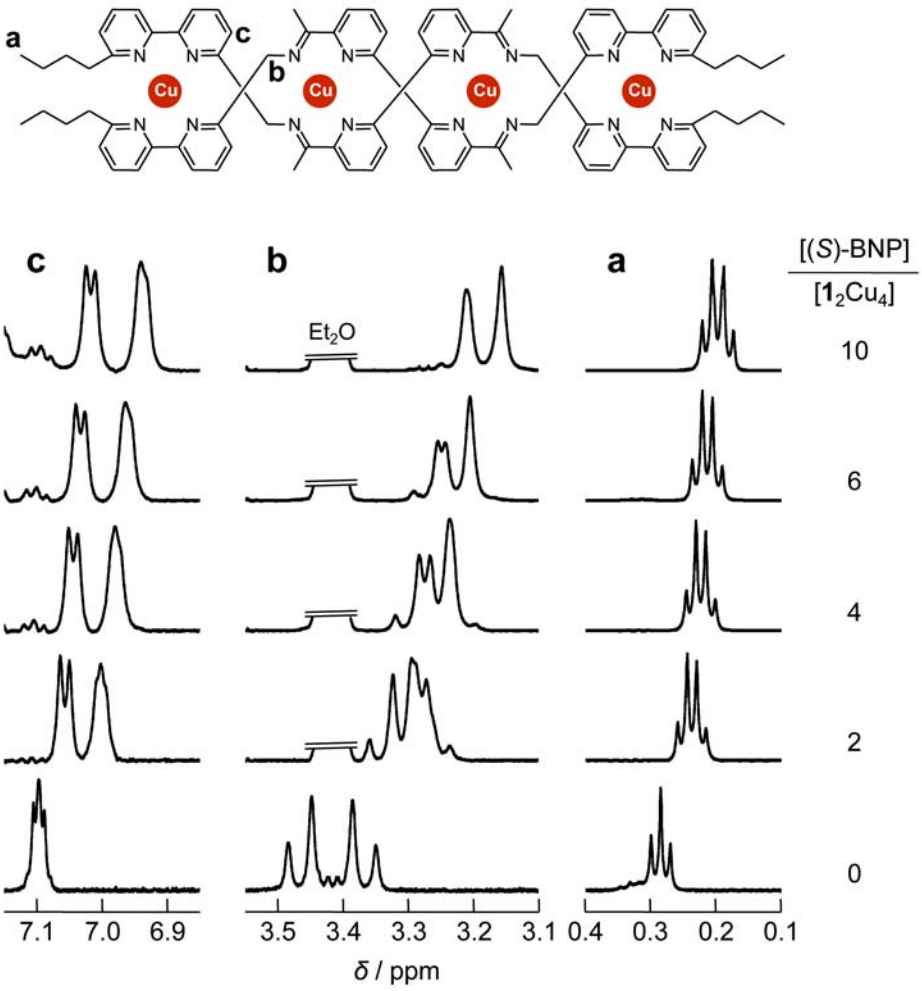



**Fig. S6.** Partial $^{1}$H NMR spectral changes at the regions of the methyl (a), methylene (b), and pyridine (c) signals of (±)-[**1**$_2$Cu$_4$](PF$_6$)$_4$ with increasing amounts of (S)-BNP·Py in $CD_2Cl_2$/$CD_3CN$ (10/1, v/v) at 25 °C; [(±)-[**1**$_2$Cu$_4$](PF$_6$)$_4$] = 1 mM.

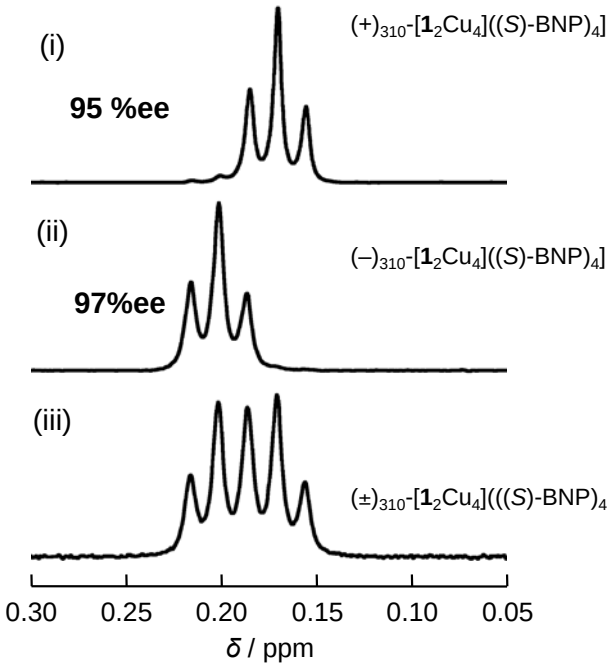



**Fig. S7.** Determination of the enantiomeric excesses (ees) of the resolved helicates. The partial $^{1}$H NMR spectra in the region of the methyl groups at both ends of $(+)_{310}$-, $(-)_{310}$-, and (±)-[**1**$_2$Cu$_4$](PF$_6$)$_4$ in the presence of (S)-BNP·py in $CD_2Cl_2$ at 25 °C; [[**1**$_2$Cu$_4$](PF$_6$)$_4$] = 0.5 mM; [(S)-BNP·py] = 20 mM.

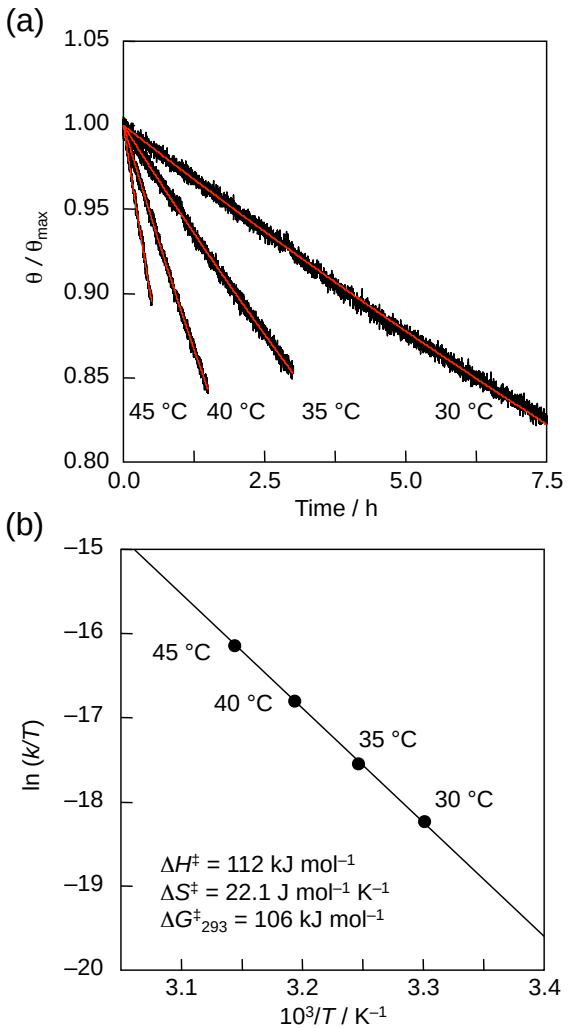



**Fig. S8.** Racemization of $(+)_{310}$-[$\mathbf{1}_2Cu_4$]$(PF_6)_4$. (a) Profiles of the CD intensities of $(+)_{310}$-[$\mathbf{1}_2Cu_4$]$(PF_6)_4$ in $CH_3CN$ at the various temperatures (30–45 °C). The red solid curves are calculated using the first-order rate equation. (b) The Eyring plots of the temperature dependence of the first-order rate constants estimated at 30 to 45 °C, from which the thermodynamic parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}_{293}$) were estimated by the least-squares curve fitting method.

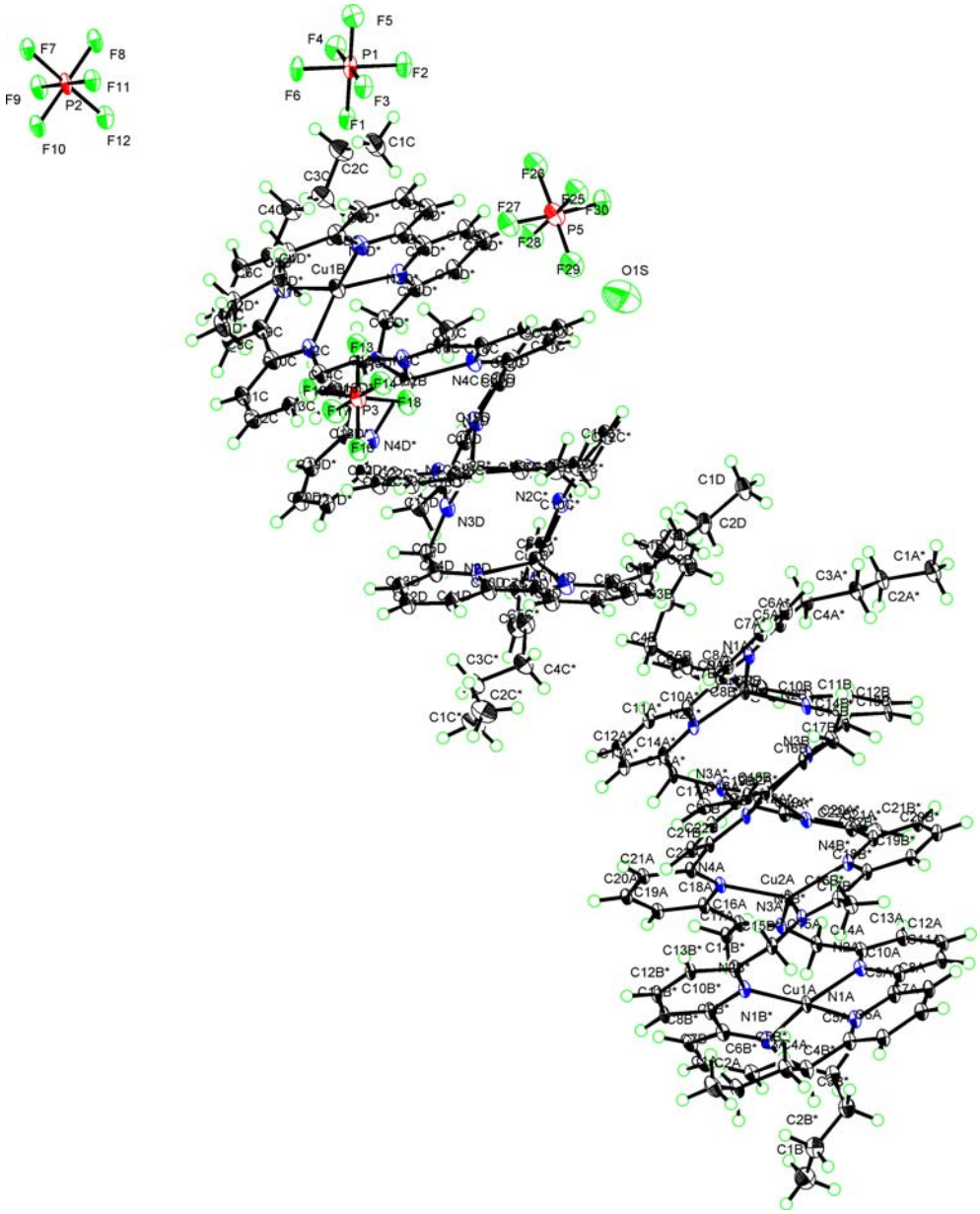


**Fig. S9.** ORTEP drawing of [$\mathbf{1}_2Cu_4$]($PF_6$)$_4$ with thermal ellipsoids at 50% probability.

**Table S1.** Crystal data and structure refinement for $[\mathbf{1}_2Cu_4](PF_6)_4$.

| | | |
|---|---|---|
| CCDC Number | 818166 | |
| Empirical formula | $(C_{88}H_{92}N_{16}Cu_4)\cdot 4(PF_6)\cdot(H_2O)$ | |
| Formula weight | 2225.86 | |
| Temperature | 90 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | *Monoclinic* | |
| Space group | *P2/c* | |
| Unit cell dimensions | $a$ = 32.027(9) Å | $\alpha$= 90° |
| | $b$ = 11.894(3) Å | $\beta$= 107.539(3)° |
| | $c$ = 24.907(7) Å | $\gamma$ = 90° |
| Volume | 9047(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.635 g cm$^{-3}$ | |
| Absorption coefficient | 1.106 mm$^{-1}$ | |
| F(000) | 4528 | |
| Crystal size | 0.60 × 0.03 × 0.01 mm$^3$ | |
| Theta range for data collection | 2.11 to 23.26° | |
| Index ranges | $-35 \le h \le 30$, $-13 \le k \le 12$, $-26 \le l \le 27$ | |
| Reflections collected | 35152 | |
| Independent reflections | 12956 [R(int) = 0.0972] | |
| Completeness to theta = 23.26° | 99.7 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 0.9890 and 0.5567 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 12956 / 1872 / 1235 | |
| Goodness-of-fit on F$^3$ | 1.168 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.1338, $wR_2$ = 0.2857 | |
| R indices (all data) | $R_1$ = 0.1791, $wR_2$ = 0.3032 | |
| Largest diff. peak and hole | 1.302 and –2.109 e·Å$^{-3}$ | |

**Table S2.** Selected distances and angles of $[\mathbf{1}_2Cu_4](PF_6)_4$.

| Cu–N lengths | | | Cu···Cu distances | | | |
|---|---|---|---|---|---|---|
| Atom 1 | Atom 2 | length/Å | Atom 1 | Atom 2 | distance/Å | |
| Cu1A | N1B | 2.03(1) | Cu1B | Cu2B | 3.386(3) | |
| Cu1A | N2B | 2.02(1) | Cu2B | Cu2B | 3.213(3) | |
| Cu1A | N2A | 2.09(1) | Cu2A | Cu1A | 3.154(3) | |
| Cu1A | N1A | 2.04(1) | Cu2A | Cu2A | 3.085(3) | |
| Cu1B | N1C | 2.01(1) | | | | |
| Cu1B | N2C | 2.01(1) | N–Cu–N chelate angles | | | |
| Cu1B | N1D | 2.03(1) | Atom 1 | Atom 2 | Atom 3 | angle/° |
| Cu1B | N2D | 2.06(1) | N1B | Cu1A | N2B | 82.2(5) |
| Cu2A | N3A | 2.04(1) | N2A | Cu1A | N1A | 82.8(5) |
| Cu2A | N4A | 2.06(1) | N3A | Cu2A | N4A | 80.7(5) |
| Cu2A | N3B | 2.05(1) | N3B | Cu2A | N4B | 80.5(5) |
| Cu2A | N4B | 2.04(1) | N1C | Cu1B | N2C | 83.0(5) |
| Cu2B | N3D | 2.00(1) | N1D | Cu1B | N2D | 82.0(5) |
| Cu2B | N4D | 2.04(1) | N4D | Cu2B | N3D | 81.8(5) |
| Cu2B | N3C | 2.03(1) | N3C | Cu2B | N4C | 80.9(5) |
| Cu2B | N4C | 2.03(1) | | | | |
| Cu1A | N1B | 2.03(1) | | | | |

## 4. Supporting references

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