Experimental Section.

General Considerations. All chemicals were obtained from Wako or Aldrich and were used as received unless otherwise indicated. Acetonitrile was distilled from CaH_2. ^1H NMR spectra were recorded at 500 MHz on JEOL Lambda-500 and were referenced to tetramethylsilane (TMS) at 0.00 ppm. ^{13}C NMR spectra were recorded at 125.65 MHz on JEOL Lambda-500 and were referenced to 77.0 ppm in chloroform-d and to tetramethylsilane (TMS) at 0.00 ppm in acetonitrile-d_3 (CD_3CN). Optical rotations were measured on JASCO DIP-1000 at Na-D line in a 1 dm cell. UV/Vis spectra were recorded on HITACHI U-3000 and CD spectra were recorded on JASCO J-820.

Preparation of square complex 3b[1] by solvent-free reaction:

A mixture of (en)Pt$(NO_3)_2$ (113.8 mg, 0.3 mmol) and 4,4'-bipyridine (46.9 mg, 0.3 mmol) was ground in a mortar at r.t. The mixture became very sticky after grinding for about 10 minutes. After 30 minutes of grinding at r.t, water (1 mL) was added to dissolve the sticky mixture. On dropwise addition of ethanol (9 mL), a lot of powder precipitated. Filtration and washing of the precipitation with ethanol followed by drying on vacuum gave a pale yellow powder (105mg, 65.4%). The mother liquor was concentrated to give a second crop (17.5 mg, 10.9%). ^1H NMR (500 MHz, D_2O, TMS in $CDCl_3$ as an external standard): δ (ppm) 2.85 (s, 16H, NCH_2CH_2N), 7.89 (d-like, J=6.7Hz, 16H, ArH_β), 8.91 (d-like, 16H, ArH_α); ^{13}C NMR (125.65 MHz, D_2O, $CDCl_3$ as an external standard), δ (ppm) 47.52 (CH2), 125.20 (C_β), 146.80 (C_γ), 152.75 (C_α).

Preparation of bowl shaped complex 5[2] by solvent-free reaction:

The bowl shaped complex **5** was prepared in the same way as **3b** and precipitated from water/methanol to give pure **5** in 90% yield. ^1H NMR (500 MHz, D_2O, TMS in $CDCl_3$ as an external standard): δ (ppm) 2.8-3.2 (m, 24H, NCH_2CH_2N), 7.8-7.9 (m, 12H) , 9.15 (d, J = 5.5Hz, 4H), 9.17-9.25 (m, 12H), 9.30 (d, J = 5.5Hz, 8H), 9.93 (brs, 4H), 10.59 (d, J = 1.5Hz, 8H). ^{13}C NMR (125.65 MHz, D_2O, $CDCl_3$ as an external standard), δ (ppm) 46.9, 127.0, 127.2, 133.7, 133.8, 140.4, 140.5, 152.3, 152.5, 155.4, 155.6, 169.1, 169.3.

Preparation of Helical Complexes (*R*)-8a and (*S*)-8a in solution:

To a solution of **6** (22.6mg) in degassed chloroform (2.0ml) was added $[(CH_3CN)_4Cu]PF_6$ (16.4mg) in degassed acetonitrile (2.0ml) under argon. The deep red solution was stirred at room temperature for 5h. The solvent was removed under reduced pressure and the residure was purified by column chromatograpgy (Al_2O_3, CH_2Cl_2/MeOH=95/5) to yield the pure complex. (*R*)-**8a**: 28.8mg (93%). ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 2.18 (s, 6H, CH_3), 3.65 (B part of an AB system, J=13.4 Hz, 2H), 3.69 (B part of an AB system, J=13.4 Hz, 2H), 3.81 (A part of an AB system, J=13.4 Hz, 2H), 3.82 (A part of an AB system, J=13.4 Hz, 2H), 4.14 (B part of an AB system, J=11.3 Hz, 2H), 4.45 (A part of an AB system, J=11.3 Hz, 2H), 6.70 (d, J=8.9 Hz, 2H, Ar), 6.75 (d, J=7.6 Hz, 2H, Ar), 6.86 (d, J=7.3 Hz, 2H, Ar), 6.98 (d, J=7.6 Hz, 2H, Ar), 7.17 (dt, J=1.2 Hz, 6.7Hz 2H, Ar), 7.27 (d, J=8.2 Hz, 2H, Ar), 7.51 (t, J=7.6 Hz, 2H, Ar), 7.53 (dt, J=7.5 Hz, 1.22H, Ar), 7.79 (d, J=8.6 Hz, 2H, Ar), 8.00 (t, J=7.6 Hz, 2H, Ar), 8.07 (t, J=7.9 Hz, 2H, Ar), 8.11 (t, J=7.6 Hz, 2H, Ar), 8.15 (d, J=8.2 Hz, 2H, Ar), 8.23 (d, J=8.2 Hz, 2H, Ar), 8.37 (d, J=8.2 Hz, 2H, Ar), 8.48 (d, J=8.2 Hz, 2H, Ar). ^{13}C NMR (125.65 MHz, CD_3CN): δ (ppm) 25.6 (CH_3), 68.0, 72.2, 72.3, 120.7, 122.1, 122.3, 122.4, 122.5, 123.4, 124.5, 125.0, 125.1, 125.4, 126.1, 127.1, 127.4, 127.7, 127.9, 128.5, 128.8, 129.0, 133.3, 135.8, 139.3, 139.6, 140.1, 140.2, 140.6, 151.7, 152.6, 152.8 , 153.3, 156.0, 156.3, 158.4, 166.6. Anal.; C, 55.30 , H, 3.68, N, 7.27; calcd for $C_{70}H_{54}Cu_2F_{12}N_8O_6P_2$, C, 55.37, H, 4.03, N, 6.87. $[\alpha]_D^{29.2}$ = +777.93 (C = 0.056, CH_3CN). UV/Vis (CH_3CN, 2.6 $\times10^{-5}$ M), λ_{max} (ε_{max}) = 240 nm (10.7×10^4) , 266 nm (4.9×10^4), 301 nm (5.9×10^4), 449 nm (5.5×10^3) . CD (C = 3.5 $\times10^{-5}$ M, CH_3CN, 0.1 cm cell): θ = -0.9, Δε = -190 (at 248 nm), θ = 1.0, Δε = 199 (at 304 nm). Solid-state CD (KBr): θ = -23.1 (at 254 nm), θ = 19.9 (at 315 nm). (*S*)-**8a**: 29.2 mg (97%): $[\alpha]_D^{29.7}$ = -817.97 (c = 0.054, CH_3CN). UV/Vis (CH_3CN, 3.5 $\times10^{-5}$ M), λ_{max} (ε_{max}) = 240 nm (10.2×10^4) , 266 nm (4.9×10^4) , 300 nm (5.9×10^4), 450 nm (5.6×10^3) . CD (c = 3.5 $\times10^{-5}$ M, CH_3CN, 0.1 cm cell): θ = 2.2, Δε = 187 (at 248 nm), θ = -2.4, Δε = -210 (at 304 nm). Solid-state CD (KBr): θ = 13.3 (at 254 nm), θ = -18.2 (at 313 nm).

Preparation of Helical Complexe (*R*)-8b:

(*R*)-**8b** was prepared in the same way as (*R*)-**8a** and obtained in 90% yield. ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 2.18 (s, 6H, CH_3), 3.56 (B part of an AB system, J=13.4Hz, 2H), 3.59 (B part of an AB system, J=13.4Hz, 2H), 3.60 (B part of an AB system, J=13.4Hz, 2H), 3.66 (B part of an AB system, J=13.4Hz, 2H), 3.68 (A part of an AB system, J=13.4Hz, 2H), 3.73 (A part of an AB system, J=13.4Hz, 2H), 3.80 (A part of an AB system, J=13.4Hz, 2H), 3.83 (A part of an AB system, J=13.4Hz, 2H), 4.11 (B part of an AB system, J=11.3Hz, 2H), 4.48 (A part of an AB system, J=11.3Hz, 2H), 6.67 (d, J=8.5Hz, 2H, Ar), 6.73 (d, J=7.6Hz, 2H, Ar), 6.75 (d, J=7.6Hz, 2H, Ar), 6.80 (d, J=7.6Hz, 2H, Ar), 6.84 (d, J=7.3Hz, 2H, Ar), 6.93 (d, J=7.6Hz, 2H, Ar), 7.15 (dt, J=1.2, 6.7Hz, 2H, Ar), 7.24 (d, J=8.5Hz, 2H, Ar), 7.46-7.58 (m, 4H, Ar), 7.70 (t, J=7.9Hz, 2H, Ar), 7.76 (d, J=8.5Hz, 2H, Ar), 7.87 (t, J=7.6Hz, 2H, Ar), 7.89 (t, J=7.6Hz, 2H, Ar), 7.90-7.99 (m, 4H, Ar), 8.06 (t, J=7.9Hz, 2H, Ar), 8.09 (t, J=7.0Hz, 2H, Ar), 8.11 (d, J=8.9Hz, 2H, Ar), 8.20 (t, J=9.5Hz, 6H, Ar), 8.30 (d, J=7.9Hz, 2H, Ar), 8.44 (d, J=8.2Hz, 2H, Ar). ^{13}C NMR (125.65MHz, CD_3CN): δ (ppm), 25.6 (CH_3), 68.0, 72.4, 72.5, 120.7 , 122.1, 122.3, 122.5, 122.5, 123.4, 124.5, 125.0, 125.1, 125.4, 126.1, 127.1, 127.4, 127.7, 127.9, 128.5, 128.9, 129.0, 129.0, 133.3, 135.8, 139.4, 139.5, 139.8, 139.8, 139.9, 140.2, 140.6, 151.4, 151.5, 151.7, 152.1, 152.7, 152.8, 153.3, 155.9, 156.0, 156.2, 158.4, 166.7. Anal.; C, 53.02 , H, 3.51, N, 7.91; calcd for $C_{94}H_{74}Cu_3F_{18}N_{12}O_8P_3$, C, 52.64, H, 3.51, N, 7.68. $[\alpha]_D^{23.1}$ = +456.67 (C = 0.043, CH_3CN). UV/Vis (CH_3CN, 2.0 $\times10^{-5}$ M), λ_{max} (ε_{max}) = 240 nm (7.6×10^4) , 266 nm (3.7×10^4) , 300 nm (4.3×10^4), 447 nm (3.8×10^3) . CD (C = 4.0 $\times10^{-5}$ M, CH_3CN, 0.1 cm cell): θ = -1.5, Δε = -123 (at 247 nm), θ = 2.2, Δε = 175 (at 313 nm). Solid-state CD (KBr): θ = -17.4 (at 254 nm), θ = 14.9 (at 317 nm).

Preparation of Helical Complexes 8 in the Absence of Solvent:

A mixture of (*R*)-**6a** (22.6 mg, 0.020 mmol) and $[(CH_3CN)_4Cu]PF_6$ (16.4 mg, 0.044mmol) was ground in a mortar in the ambient atmosphere, and the colour turned to deep red immediately. After 5 minutes, the red mixture was washed with benzene (10 mL), and unreacted (*R*)-**6a** (1.6 mg, 6%) was recovered from filtrate after evaporation.

Subjection of the residual solid to column chromatography (neutral Al_2O_3, CH_2Cl_2/MeOH = 95/5) provided (*R*)-**8a** (29.0mg, 94%) in a pure form. $[\alpha]_D^{29.2}$ = +777.93 (*c* = 0.056, CH_3CN). UV/Vis (CH_3CN, 2.6 $\times 10^{-5}$ M), λ_{max} (ε_{max}) = 240 nm (10.7×10^4) , 266 nm (4.9×10^4) , 301 nm (5.9×10^4), 449 nm (5.5×10^3). CD (c = 3.5 $\times 10^{-5}$ M, CH_3CN, 0.1 cm cell): θ = -0.9, $\Delta\varepsilon$ = -190 (at 248 nm), θ = 1.0, $\Delta\varepsilon$ = 199 (at 304 nm). Solid-state CD (KBr): θ = -17.4 (at 254 nm), θ = 14.9 (at 317 nm).

(*S*)-**8a:** (*S*)-8a: $[\alpha]_D^{29.7}$ = -817.97 (c = 0.054, CH_3CN). UV/Vis (CH_3CN, 3.5 $\times 10^{-5}$ M), λ_{max} (ε_{max}) = 240 nm (10.2×10^4) , 266 nm (4.9×10^4) , 300 nm (5.9×10^4), 450 nm (5.6×10^3) . CD (c = 3.5 $\times 10^{-5}$ M, CH_3CN, 0.1 cm cell): θ = 2.2, $\Delta\varepsilon$ = 187 (at 248 nm), θ = -2.4, $\Delta\varepsilon$ = -210 (at 304 nm). Solid-state CD (KBr): θ = 15.7 (at 254 nm), θ = -18.0 (at 315 nm).

(*R*)-**8b**: A mixture of (*R*)-**6b** (30.0 mg, 0.020 mmol) and $[(CH_3CN)_4Cu]PF_6$ (24.6 mg, 0.066 mmol) was ground in a mortar in the ambient atmosphere, and the colour turned to deep red immediately. After 5 minutes, the red mixture was washed with benzene (10 mL), and unreacted (*R*)-**6b** (1.5 mg, 5%) was recovered from filtrate after evaporation. Subjection of the residual solid to column chromatography (neutral Al_2O_3, CH_2Cl_2/MeOH = 95/5) provided (*R*)-**8b** (39.1 mg, 92%) in a pure form. $[\alpha]_D^{23.1}$ = +456.67 (c = 0.043, CH_3CN). UV/Vis (CH_3CN, 2.0 $\times 10^{-5}$ M), λ_{max} (ε_{max}) = 240 nm (7.6×10^4) , 266 nm (3.7×10^4) , 300 nm (4.3×10^4), 447 nm (3.8×10^3) . CD (c = 4.0 $\times 10^{-5}$ M, CH_3CN, 0.1 cm cell): θ = -1.5, $\Delta\varepsilon$ = -123 (at 247 nm), θ = 2.2, $\Delta\varepsilon$ = 175 (at 313 nm). Solid-state CD (KBr): θ = -21.6 (at 250 nm), θ = 17.3 (at 317 nm).

Solid-state CD spectra measurement (representative):

A mixture of (*R*)-**6a** (22.6 mg, 0.020 mmol) and $[(CH_3CN)_4Cu]PF_6$ (16.4 mg, 0.044mmol) was ground in a mortar in the ambient atmosphere, and the colour turned to deep red immediately. After 5 minutes, the red solids were subjected to CD measurement in Nujol mull.

References

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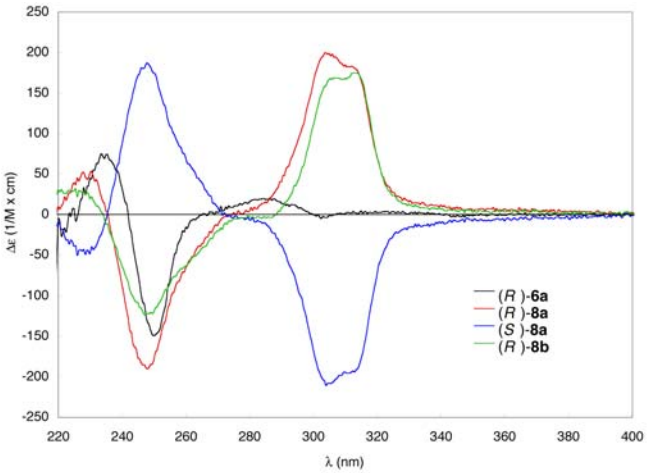

CD spectra of **6** and **8** prepared in solution.
CD spectra were measured in $CHCl_3$ at room temperature.