Supplementary Information for

On the influence of porphyrin π - π stacking on supramolecular chirality created in the porphyrin-based twisted tape structure

Masayuki Takeuchi,* Satoshi Tanaka and Seiji Shinkai*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan

e-mail: taketcm@mbox.nc.kyushu-u.ac.jp, seijitcm@mbox.nc.kyushu-u.ac.jp

Experimental:

General. All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals, Wako Organic Chemicals, or Aldrich and used as received. The ¹H NMR spectra were recorded either on a Brucker AC 250 (250 MHz) or Brucker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. Mass spectral data were obtained using a Perseptive Voyager RP MALDI TOF mass spectrometer and/or a JEOL JMS HX110A high-resolution magnetic sector FAB mass spectrometer. UV-Vis spectra were recorded with a Shimadzu UV-2500 PC spectrophotometer.

Powder X-ray Diffraction. The sample was prepared in a sample tube and frozen by liquid nitrogen. The frozen specimen was evaporated by a vacuum pump at 0.6 mmHg for 1 day at room temperature. The obtained xerogel was put into a glass capillary ($\Phi = 0.3$ mm). X-ray diffractograme was recorded on an imaging plate using Cu radiation ($\lambda = 1.54178$ Å at a distance of 15 cm).

SEM Observation. The sample was prepared in a sample tube and frozen by liquid nitrogen. The frozen specimen was evaporated by a vacuum pump at 0.6 mmHg for 1 day at room temperature. The obtained sample was shielded with platina. The accelerating voltage of SEM was 25 kV, and the emission current was 10 μ A.

TEM Observation. A piece of the sample was placed on a carbon-coated copper grid. The

specimen was evaporated by a vacuum pump at 0.6 mmHg for 1day at room temperature. The accelerating voltage of TEM was 120 kV, and the beam current was 65 μ A.

Synthesis. Compounds **1-2H**, **1-Cu**, and **1-Ni** were synthesized according to Schemes S1 and S2 and identified by ¹H NMR, high-resolution FAB-Mass measurements, and/or elemental analyses.



Fig. S1 UV-Vis spectra of **1-Cu** (1.0 $\times 10^{-6}$ M) and **1-Ni** (1.0 $\times 10^{-6}$ M) in THF (solid line) and assembly of **1-Cu** (1.00 wt %) and **1-Ni** (1.00 wt %) prepared from *t*-butanol (dotted line) at 25 °C.



Fig. S2 XRD patterns of the freeze-dried suspended solids prepared from *t*-butanol of **1-Cu** (1.00 wt %) and **1-Ni** (1.00 wt %).



Fig. S3 (A) Structure of the *N*-methylaminomethyl moiety estimated from computational energy-minimization (Insight II, Discover-3). (b) Molecular models for the mirror image of the *N*-methylaminomethyl moiety.

Synthesis

Scheme S1



Scheme S2



5,15-Bis(3,5-di-*n*-dodecyloxyphenyl)porphyrin (3). 2,2'-Dipyrromethane (1.64 g, 11.2 mmol) and **2** (5.32 g, 11.2 mmol) were dissolved in CH₂Cl₂ (2.2 L). After addition of trifluoroacetic acid (0.60 ml), the solution was stirred for 4 h at room temperature under N₂ in the dark. Then, DDQ (3.26 g, 14.4 mmol) was added to the solution and the reaction mixture was stirred for 30 min. The reaction mixture was passed through silica pad [CHCl₃] directly. Further purification by column chromatography [silica gel, CHCl₃/*n*-hexane = 1:1 (v/v)] was gave **3** in 36 % (2.41 g) as purple solid: mp. 73.1-73.4 °C; ¹H-NMR (250 MHz, CDCl₃, TMS, rt) d -3.16 (s, 2H), 0.85 (t, *J* = 6.0, 12H), 1.24 (m, 64H), 1.51 (m, 8H), 1.88 (m, 8H), 4.15 (t, *J* = 6.5, 8H), 6.92 (s, 2H), 7.42 (d, *J* = 2.0, 4H), 9.19 (d, *J* = 4.6, 4H), 9.37 (d, *J* = 4.7, 4H), 10.29 (s, 2H); MALDI-TOF-MS [dithranol] *m*/z calcd for [M+H]⁺ = 1200.92, found 1200.82; Anal. Calcd for C₈₀H₁₁₈N₄O₄: C, 80.08; H, 9.91; N, 4.67. Found: C, 79.99; H, 9.88; N, 4.61.

5,15-Dibromo-10,20-bis(**3,5-di***n***-dodecyloxyphenyl**)**porphyrinatozinc** (**5**). Compound **3** (2.0 g, 1.67 mmol) was dissolved in CHCl₃ (400 ml), and cooled to 0 °C. NBS (594 mg, 3.34 mmol) and pyridine (1.5 ml) were added to the solution, and the mixture was stirred for 15 min at 0 °C. The reaction progress was monitored by TLC [silica gel, CHCl₃ /*n*-hexane = 1:1 (v/v)]. The reaction was

quenched with acetone (30 ml) and the solution was concentrated under reduced pressure. The resulting residue was subjected to column chromatography [silica gel, CHCl₃/*n*-hexane = 1:1 (v/v)] to give **4** as purple solid. After confirming the formation of **4** by ¹H-NMR and MALDI-TOF-MS, we used **4** for the synthesis of **5**. Compound **4** was dissolved in CHCl₃ (400 ml). After addition of the methanol solution (100 ml) of Zn(OAc)₂•2H₂O (3.67 g, 16.7 mmol), the mixture was stirred for 1 h at room temperature. The solution was concentrated under reduced pressure and the resulting residue was washed with water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give **5** in 94 % from **3** (2.24 g) as purple solid: **4**; ¹H-NMR (250 MHz, CDCl₃,TMS, rt) d -2.76 (s, 2H), 0.85 (t, *J* = 6.9, 12H), 1.24 (m, 64H), 1.53 (m, 8H), 1.87 (m, 8H), 4.12 (t, *J* = 6.6, 8H), 6.90 (s, 2H), 7.31 (d, *J* = 2.1, 4H), 8.95 (br, 4H), 9.60 (d, *J* = 4.5, 4H); MALDI-TOF-MS [dithranol] *m/z* calcd for [M+H]⁺ = 1358.77, found 1358.61. **5**; mp. 192.0-195.4 °C; ¹H-NMR (250 MHz, CDCl₃, TMS, rt) d 0.85 (m, 12H), 1.23 (m, 64H), 1.49 (m, 8H), 1.87 (m, 8H), 4.12 (t, *J* = 6.6, 8H), 6.89 (s, 2H), 7.31 (s, 4H), 9.07 (d, *J* = 4.7, 4H), 9.72 (d, *J* = 4.7, 4H); MALDI-TOF-MS [dithranol] *m/z* calcd for [M+H]⁺ = 1421.69, found 1421.98.; Anal. Calcd for C₈₀H₁₁₄Br₂N₄O₄Zn: C, 67.62; H, 8.09; N, 3.94. Found: C, 67.76; H, 8.21; N, 3.93.

Compound 6. Compound **5** (1.31 g, 0.92 mmol), **9**^[11] (129 mg, 0.46 mmol), Pd(PPh₃)₂Cl₂ (64.7 mg, 92.2 mmol), and CuI (26.3 mg, 0.14 mmol) were mixed in dry triethylamine (70 ml). The mixture was stirred for 3 h at room temperature under N₂. The reaction progress was monitored by TLC [silica gel, CHCl₃]. The solution was concentrated under reduced pressure and the resulting residue was washed with saturated ammonium chloride and water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was subjected to column chromatography [silica gel, CHCl₃] to give **6** in 25 % (374 mg) as green soild: mp. 190.0-191.0 °C; ¹H-NMR (600 MHz, CDCl₃, TMS, rt) d 0.84 (t, *J* = 6.9, 12H), 1.23-1.31 (m, 56H), 1.37 (m, 8H), 1.50 (m, 8H), 1.87 (m, 8H), 3.08 (s, 3H), 3.89 (s, 3H), 4.13 (t, *J* = 6.6, 8H), 4.58 (s, 2H), 6.65 (d, *J* = 8.3, 2H), 6.89 (s, 2H), 7.29 (d, *J* = 8.1, 2H), 7.34 (d, *J* = 1.7, 4H), 7.64 (d, *J* = 8.3, 2H), 8.00 (d, *J* = 8.2, 2H), 9.02 (m, 4H), 9.65 (d, *J* = 4.6, 2H), 9.69 (d, *J* = 4.4, 2H); MALDI-TOF-MS [dithranol] *m/z* calcd for [M+H]⁺ = 1620.75, found 1620.40.; Anal. Calcd for

C₉₈H₁₃₀BrN₅O₆Zn: C, 72.68; H, 8.09; N, 4.32. Found: C, 72.68; H, 8.15; N, 4.30.

Compound 8. Compound 6 (350 mg, 0.22 mmol), 4-ethynylpyridine (66.8 mg, 0.65 mmol), Pd(PPh₃)₂Cl₂ (15.2 mg, 21.6 mmol), and CuI (6.2 mg, 32 mmol) were mixed in dry triethylamine (15 ml). The mixture was stirred for 12 h at 70 °C under N₂. The reaction progress was monitored by TLC (silica gel, CHCl₃). The solution was concentrated under reduced pressure and the resulting residue was washed with saturated ammonium chloride and water. The organic layer was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The resulting residue was subjected to column chromatography [silica gel, $CHCl_3/n$ -hexane = 3:1 (v/v)] to give 7 in 86 % yield (306 mg) as green solid. Compound 7 (300 mg, 0.18 mmol) was dissolved in CH₂Cl₂ (80 ml). After addition of TFA (0.80 ml), the solution was stirred for 1 h at room temperature. The reaction mixture was washed with 5 % aqueous NH₄OH and water and the organic layer was dried over anhydrous Na₂SO₄. The solution was concentrated under reduced pressure. The resulting residue was subjected to column chromatography on silica gel (CHCl₃) to give 8 (234 mg, 81 %) as green solid. 7; ¹H-NMR (600 MHz, pyridine- d_5 , TMS, rt) d 0.84 (t, J = 6.9, 12H), 1.23-1.30 (m, 56H), 1.36 (m, 8H), 1.55 (m, 8H), 1.93 (m, 8H), 3.07 (s, 3H), 3.84 (s, 3H), 4.23 (t, J = 6.4, 8H), 4.71 (s, 2H), 7.03 (d, J = 8.7, 2H), 7.35 (s, 2H), 7.41 (t, J = 8.2, 2H), 7.76 (d, J = 2.0, 4H), 7.97 (d, J = 5.6, 2H), 8.17(d, J = 8.5, 2H), 8.19 (d, J = 8.3, 2H), 8.95 (d, J = 5.5, 2H), 9.36 (d, J = 4.4, 2H), 9.42 (d, J = 4.4, 2H), 9.2H), 10.08 (d, J = 4.5, 2H), 10.17 (d, J = 4.4, 2H); MALDI-TOF-MS [dithranol] m/z calcd for [M+H]⁺ = 1642.95, found1642.61. **8**; mp. 131.2-132.1 °C; ¹H-NMR (600 MHz, CDCl₃, TMS, rt) d -1.88 (s, 2H), 0.84 (t, J = 6.9, 12H), 1.23-1.31 (m, 56 H), 1.37 (m, 8H), 1.51 (m, 8H), 1.88 (m, 8H), 3.22 (s, 3H), 3.93 (s, 3H), 4.14 (t, J = 6.6, 8H), 4.74 (s, 2H), 6.88 (d, J = 8.7, 2H), 6.90 (s, 2H), 7.34 (d, J = 1.6, 4H), 7.36 (d, J = 8.2, 2H), 7.85 (d, J = 5.3, 2H), 7.88 (d, J = 8.9, 2H), 8.05 (d, J = 8.2, 2H), 7.88 (d, J = 8.9, 2H), 8.05 (d, J = 8.2, 2H), 8.2H), 8.82 (d, J = 5.0, 2H), 8.91 (d, J = 4.2, 2H), 8.96 (d, J = 4.3, 2H), 9.58 (d, J = 4.6, 2H), 9.64 (d, J = 4.6, J = 4.5, 2H; HR-FAB [NBA] m/z calcd for [M]⁺ = 1577.0521, found 1577.0427.

1-2H. Compound **8** (130 mg, 82.4 mmol) was dissolved in THF (20 ml). KOH (2.0 ml, 2 M in $H_2O/MeOH = 4:1$ (v/v)) was added and the mixture was refluxed for 24 h. The reaction progress was monitored by TLC [silica gel, CHCl₃/MeOH = 25:1 (v/v)]. After cooling the mixture to room

temperature, the solution was concentrated under reduced pressure. The resulting residue was washed with water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was subjected to column chromatography [silica gel, CHCl₃/MeOH = 25:1 (v/v)] to give **1-2H** in 84 % (108 mg) as green solid: mp. 166.7-168.0 °C; ¹H-NMR (600 MHz, CD₂Cl₂ / pyridine- d_5 , TMS, rt) d -1.69 (s, 2H), 0.83 (t, *J* = 6.9, 12H), 1.23-1.35 (m, 56H), 1.37 (m, 8H), 1.52 (m, 8H), 1.89 (m, 8H), 3.12 (s, 3H), 4.17 (t, *J* = 6.5, 8H), 4.69 (s, 2H), 6.93 (d, *J* = 8.6, 2H), 7.08 (s, 2H), 7.37 (d, *J* = 8.2, 2H), 7.46 (d, *J* = 1.8, 4H), 7.85 (d, *J* = 5.5, 2H), 7.97 (d, *J* = 8.5, 2H), 8.26 (d, *J* = 8.2, 2H), 8.82 (d, *J* = 5.4, 2H), 9.03 (d, *J* = 4.4, 2H), 9.08 (d, *J* = 4.5, 2H), 9.73 (d, *J* = 4.7, 2H), 9.81 (d, *J* = 4.6, 2H); HR-FAB [NBA] *m*/z calcd for [M]⁺ = 1563.0365, found 1563.0363.

1-Cu. Compound **1-2H** (98 mg, 63 mmol) was dissolved in CHCl₃ (20 ml). After addition of the methanol solution (5 ml) of Cu(OAc)₂•H₂O (126 mg, 0.63 mmol), the solution was stirred for 5 h at room temperature. The mixture was concentrated under reduced pressure and the resulting residue was washed with saturated ammonium chloride aqueous solution and water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was subjected to column chromatography [silica gel, CHCl₃/MeOH = 10:1 (v/v)] to give **1cp-Cu** in 29 % (30 mg) as green solid: mp. 235.6-236.9 °C; HR-FAB [NBA] *m/z* calcd for [M]⁺ = 1618.9562, found 1618.9531; Anal. Calcd for C₁₀₄H₁₃₂CuN₆O₆•0.50H₂O: C, 76.41; H,8.20; N, 5.14. Found: C, 76.12; H, 8.20; N, 5.03.

Compound 8-Ni. Compound **8** (98 mg, 63 mmol) was dissolved in CHCl₃ (65 ml). After addition of the methanol solution (50 ml) of Ni(OAc)₂•4H₂O (1.24 g, 5.08 mmol), the mixture was refluxed for 6 days. The solution was concentrated under reduced pressure and the resulting residue was washed with saturated sodium hydrogen carbonate aqueous solution and sodium chloride aqueous solution. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was subjected to column chromatography (silica gel, CHCl₃) to give **8-Ni** in 97 % (201 mg) as green solid: mp. 130.0-133.0 °C; ¹H-NMR (600 MHz, CDCl₃, TMS, rt) d 0.85 (t, J = 6.9, 12H), 1.23-1.30 (m, 56 H), 1.36 (m, 8H), 1.48 (m, 8H), 1.85 (m, 8H), 3.19 (s, 3H),

3.92 (s, 3H), 4.08 (t, J = 6.6, 8H), 4.72 (s, 2H), 6.88 (m, 2H+2H), 7.14 (d, J = 2.0, 4H), 7.34 (d, J = 8.2, 2H), 7.76 (d, J = 5.5, 2H), 7.78 (d, J = 8.6, 2H), 8.04 (d, J = 8.2, 2H), 8.77 (br, 2H), 8.81 (d, J = 4.9, 2H), 8.85 (d, J = 4.8, 2H), 9.44 (d, J = 4.9, 2H), 9.50 (d, J = 4.9, 2H); HR-FAB [NBA] m/z calcd for [M]⁺ = 1632.9718, found 1632.9725.

1-Ni. Compound **8-Ni** (100 mg, 61.2 mmol) was dissolved in THF (16 ml). KOH (1.6 ml, 2 M in $H_2O/MeOH = 4:1$ (v/v)) was added and the mixture was refluxed for 12 h. The reaction progress was monitored by TLC [silica gel, CHCl₃/MeOH = 10:1 (v/v)]. After cooling the mixture to room temperature, the solution was concentrated under reduced pressure. The resulting residue was washed with water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting residue was subjected to column chromatography [silica gel, CHCl₃/MeOH = 10:1 (v/v)] to give **1-Ni** in 87 % (86 mg) as green solid: mp. 198.0-200.0 °C; ¹H-NMR (600 MHz, THF-*d*₈, TMS, rt) d 0.74 (t, *J* = 6.9, 12H), 1.15-1.26 (m, 56H), 1.29 (m, 8H), 1.41 (m, 8H), 1.72 (m, 8H), 3.08 (s, 3H), 4.00 (t, *J* = 6.5, 8H), 4.67 (s, 2H), 6.76 (s, 2H), 6.81 (d, *J* = 8.8, 2H), 7.08 (d, *J* = 2.0), 7.25 (d, *J* = 8.2, 2H), 7.67 (d, *J* = 8.6, 2H), 7.74 (d, *J* = 4.5, 2H), 7.89 (d, *J* = 8.2, 2H), 8.80 (d, *J* = 4.8, 2H), 8.85 (d, *J* = 4.8, 2H), 9.50 (d, *J* = 4.7, 2H), 9.52 (d, *J* = 4.9, 2H); HR-FAB [NBA] *m/z* calcd for [M]⁺ = 1623.9504, found 1623.9515.

References

[1] S. Tanaka, M. Shirakawa, K. Kaneko, M. Takeuchi, S. Shinkai, S. Langmuir 2005, 21, 2163-2172.