Chiroptical Sensing of Asymmetric Hydrocarbons Using a Homochiral Supramolecular Box from a Bismetalloporphyrin Rotamer

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1. Measurements

Circular dichroism (CD), electronic absorption, and fluorescence spectra were recorded on a JASCO type J-820 spectropolarimeter equipped with a JASCO type PTC-423L temperature/stirring controller, a JASCO type V-570 UV/VIS/NIR spectrometer equipped with a JASCO type ETC-505T temperature/stirring controller, and a JASCO type FP–777W spectrometer equipped with a JASCO type ECT-271 temperature/stirring controller, respectively. $^1$H NMR spectra were recorded on a JEOL model EX–270 or GSX–500 spectrometer, where chemical shifts ($\delta$ in ppm) were determined with respect to tetramethylsilane (TMS) as an internal standard. Preparative size-exclusion chromatography (SEC) was carried out on a Japan Analytical Industry model LC–908 recycling preparative HPLC equipped with a column set consisting of JAIGEL–2H (exclusion limit $5 \times 10^3$) and JAIGEL–3H (exclusion limit $3 \times 10^4$), using CHCl$_3$ as an eluent at a flow rate of 3.5 mL min$^{-1}$. Matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF-MS) spectrometry was performed with 9-nitroanthracene as a matrix on an Applied Biosystems BioSpectrometry Workstation$^{TM}$ model Voyager-DE$^{TM}$ STR spectrometer. Analytical chiral HPLC was performed at 20 $^\circ$C using CH$_2$Cl$_2$/hexane (3:7) as an eluent on a SUMICHIRAL OA-3100 column (4.6 mm-$\phi$ × 250 mm) using a JASCO Type PU-980 HPLC pump, equipped with JASCO Type UV-970 variable-wavelength UV/Vis detector and CD-2095A CD detector.
2. Synthesis

5-(4-Pyridyl)-10-(trimethylsilylbutadinylo)-15-(3,5-didodecyloxyphenyl)porphyrin (4)

To a CH$_2$Cl$_2$ solution (50 mL) of the zinc complex of 5-(4-pyridyl)-15-(3,5-didodecyloxyphenyl)-10-(trimethylsilylethynyl)porphyrin (3)$^{[1,2]}$ (196 mg, 198 µmol) was added a THF solution of Bu$_4$NF (1.0 M, 200 µL), and the mixture was stirred for 1 h at room temperature. Then, the reaction mixture was extracted with CHCl$_3$/water, and the combined organic extract was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness. The residue was recrystallized from CH$_2$Cl$_2$/MeCN to give green solid. To a CH$_2$Cl$_2$/pyridine (100:1) solution (500 mL) of this residue were successively added trimethylsilylacetylene (TMSA; 1.0 mL, 17.2 mmol), tetramethylethylenediamine (TMEDA; 1.38 g, 11.9 mmol), and CuCl (1.18 g, 11.9 mmol), and the mixture was stirred for 15 min at room temperature. Then, the reaction mixture was extracted with CHCl$_3$/water, and the combined organic extract was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness. A CHCl$_3$ solution of the residue was treated with 6 N aq. HCl, washed with aq. NaHCO$_3$ and water, dried over anhydrous Na$_2$SO$_4$, and then evaporated to dryness. The residue was subjected to size exclusion chromatography (SEC) with toluene as an eluent, where the second fraction was collected and recrystallized from CH$_2$Cl$_2$/MeCN, to give 4 as green solid in 39%...
yield (74 mg, 77 µmol). MALDI–TOF MS m/z 952, [M + H]+ calcd for C_{60}H_{77}N_{5}O_{2}Si 952; 1H NMR (270 MHz, CDCl₃): δ (ppm) –2.66 (s, NH), 0.39 (s, TMS), 0.83 (t, J = 6.8 Hz, Me), 1.22–1.45 (br. alkyl), 1.70 (t, J = 6.8 Hz, alkyl), 4.13 (t, J = 6.8 Hz, alkyl), 6.90 (s, Ar), 7.33 (d, J = 1.6 Hz, Ar), 8.14 (d, J = 5.1 Hz, Py), 8.84 (d, J = 5.0 Hz, pyrrole-β), 8.87 (d, J = 5.0 Hz, pyrrole-β), 9.03 (d, J = 5.0 Hz, pyrrole-β), 9.06 (d, J = 5.1 Hz, Py), 9.25 (d, J = 5.0 Hz, pyrrole-β), 9.28 (d, J = 5.0 Hz, pyrrole-β), 9.66 (d, J = 5.0 Hz, pyrrole-β), 9.70 (d, J = 5.0 Hz, pyrrole-β), and 10.17 (s, meso).

Non-assembling reference of 1 without pyridyl groups (1_REF)

To a CH₂Cl₂ solution (50 mL) of the zinc complex of 5,15-(3,5-didodecyloxyphenyl)-10-(trimethylsilyl ethynyl)porphyrin (5)¹ ² (621 mg, 0.46 mmol) was added a THF solution of Bu₄NF (1.0 M, 1.0 mL), and the mixture was stirred for 1 h at room temperature. The reaction mixture was extracted with CHCl₃/water, and the combined organic extract was dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was recrystallized from CH₂Cl₂/MeCN to give green solid. To a CH₂Cl₂ solution (500 mL) of this solid residue were successively added trimethylsilylacetylene (TMSA; 1.0 mL, 17.2 mmol), tetramethylethylenediamine (TMEDA; 0.75 mL, 4.97 mmol), and CuCl (500 mg, 5.05 mmol), and the mixture was stirred for 15 min at room temperature. Then, the reaction mixture was extracted with
CHCl3/water, and the combined organic extract was dried over anhydrous Na2SO4 and evaporated to dryness. The residue was subjected to size exclusion chromatography (SEC) with toluene as an eluent, where the second fraction was collected and recrystallized from CH2Cl2/MeCN to give green solid (38 mg). To a CH2Cl2 solution (15 mL) of this residue was added a THF solution of Bu4NF (1.0 M, 100 µL), and the mixture was stirred for 1 h at room temperature. Then, the reaction mixture was extracted with CHCl3/water, and the combined organic extract was dried over anhydrous Na2SO4, and evaporated to dryness. The residue was recrystallized from CH2Cl2/MeCN to give green solid. To a CH2Cl2 solution (100 mL) of this residue were successively added TMEDA (0.34 mL, 2.24 mmol) and CuCl (220 mg, 2.24 mmol), and the mixture was stirred for 15 min at room temperature. Then, the reaction mixture was washed with water and extracted with CH2Cl2, and the combined organic extract was dried over anhydrous Na2SO4 and evaporated to dryness. The residue was subjected to size exclusion chromatography (SEC) with toluene as an eluent, where the first fraction was collected and recrystallized from CH2Cl2/MeCN, to give 1Ref as green solid in 4% yield (23 mg, 8.8 µmol). MALDI–TOF MS m/z 2620, [M + H]+ calcd for C168H230N8O8Zn2 2620; UV/Vis (CHCl3): λmax = 431, 461, 489, 640, and 659 nm; 1H NMR (500 MHz, CDCl3): δ (ppm) 0.83 (t, J = 6.7 Hz, 24H, Me), 1.23–1.38 (br. 144H, alkyl), 1.89 (t, J = 7.5 Hz, 16H, alkyl), 4.15 (t, J = 6.5 Hz, 16H, alkyl), 6.90 (s, 4H, Ar), 7.36 (d, J = 1.83 Hz, 8H, Ar), 9.09 (d, J = 5.0 Hz, 4H, pyrrole-β), 9.16 (d, J = 5.0 Hz, 4H, pyrrole-β), 9.30 (d, J = 5.0 Hz, 4H, pyrrole-β), 9.73 (d, J = 5.0 Hz, 4H, pyrrole-β), and 10.18 (s, 2H, meso).
3. Characterization of box-shaped cyclic tetramer

Similar to the case of 2 [see refs. 1–3], cyclic tetramerization of tetraalkynylene-linked zinc porphyrin dimer 1 was confirmed.

3-1. Size-exclusion chromatography of self-assembled 1 and reference compounds

![Diagram of molecules 1, 2, and 1Ref with size-exclusion chromatogram](image)

**Figure S1.** Size-exclusion chromatogram (SEC; CHCl₃ as an eluent) of self-assembled 1, along with those of its dialkynylene analogue 2 and non-assembling reference 1Ref.

→ It is reasonable that the retention time of self-assembled 1 is slightly shorter than that of a previously reported cyclic tetramer of 2 and much shorter than that of a non-assembling reference 1Ref.
3-2. $^1$H NMR spectroscopy of self-assembled 1

**Figure S2.** $^1$H NMR spectrum (500 MHz) of self-assembled 1 in CDCl$_3$ at 20 °C. Ar: aryl, Py: pyridyl.

→ The two sets of pyridyl signals at $\delta$ 2–3 and 6–7 ppm (square blankets) are characteristic of the formation of cyclic tetramers BOX$_\perp$ and BOX$_\parallel$. The integral ratio of the signal at $\delta$ 10.06 to that at 10.05 ppm, both due to meso-H, is nearly unity, indicating a 1:1 ratio of BOX$_\perp$ to BOX$_\parallel$. 
3-3. Absorption and emission spectroscopies of self-assembled 1

![Diagram of BOX⊥ and BOX∥](image)

**Absorption spectrum of 1**
A mixture of BOX⊥ and BOX∥

**Absorption spectra**
- **BOX⊥**: Separated as the first fraction in chiral HPLC
- **BOX∥**: Differential spectrum by subtraction of the spectral profile of BOX⊥ from a)

**Fluorescence spectra**
Selective photoexcitation of BOX⊥ and BOX∥
- **BOX⊥**: Excitation at 458 nm
- **BOX∥**: Excitation at 500 nm

**Fluorescence excitation spectra**
- **BOX⊥**: Monitored at 644 nm
- **BOX∥**: Monitored at 700 nm
These excitation spectra are analogous to the absorption spectra of BOX⊥ and BOX∥, respectively, in b).

**Figure S3.** a and b) Absorption, c) fluorescence, and d) fluorescence excitation spectra of self-assembled 1 in CH₂Cl₂/hexane (3:7) at 20 °C.

→ All the spectral characteristics are consistent with one another, and reasonably reflect the extents of π-electronic conjugation in BOX⊥ (twisted geometry) and BOX∥ (parallel geometry).
4. Absorption spectroscopy of 1 in limonene and CHCl₃

![Absorption spectra of 1 in limonene and CHCl₃](image)

**Figure S4.** Absorption spectra of self-assembled 1 ([1] = 6.92 × 10⁻⁶ M) at 20 °C in (R)-limonene (red curve) and CHCl₃ (blue curve).

In CHCl₃, the ratio of the absorbances at 638 and 666 nm, due to BOX⊥ and BOX∥, respectively, was 51:49, which is in excellent agreement with the ratio [BOX⊥]/[BOX∥] determined by ¹H NMR spectroscopy. Assuming that the ratio of these two absorbances in limonene also reflects the relative abundance of BOX⊥ to BOX∥ properly, [BOX⊥]/[BOX∥] is estimated as 38:62.
5. References

