

Supplementary Information

Cyclic dimer of a fused porphyrin zinc complex as a novel host with two π -electronically coupled binding sites

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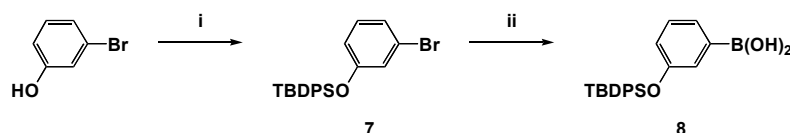
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1. Measurements

Electronic absorption spectra were recorded on a JASCO model U-best V-560 or V-570 spectrometer. ^1H NMR spectra were recorded at 293 K in CDCl_3 or toluene- d_8 on a JEOL Type GSX-270 spectrometer, operating at 270.05 MHz, using a residual non-deuterated solvent as an internal reference. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on an Applied Biosystems BioSpectrometry WorkstationTM model Voyager-DETM STR spectrometer using dithranol as a matrix.

2. Synthesis

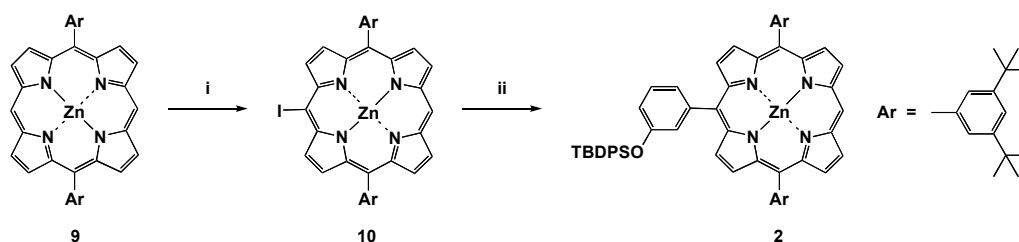
2-1. Synthesis of boronic acid 8



Scheme 1. Reagents and conditions: (i) TBDPSCl, imidazole, DMF, r.t.; (ii) *n*-BuLi, B(OMe)₃, THF, $-78\text{ }^\circ\text{C}$.

8: To a DMF solution (350 mL) of a mixture of 3-bromophenol (25 g, 0.14 mol) and imidazole (10 g, 0.15 mol) was dropwise added *tert*-butyldiphenylsilyl chloride (TBDPSCl; 40 mL, 0.15 mol), and the mixture was stirred for 2 h under Ar at room temperature. Then, the reaction mixture was poured into toluene, and the solution was washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was chromatographed on silica gel with CHCl_3 as an eluent, where the first fraction was collected and evaporated to leave **7** as colorless transparent oil (58 g, 98%). To a THF solution (80 mL) of **7** (10 g, 24 mmol) was dropwise added a hexane solution of *n*-BuLi (1.5 M, 19 mL), and the mixture was stirred for 2 h at $-78\text{ }^\circ\text{C}$ under Ar. To the reaction mixture was dropwise added $\text{B}(\text{OMe})_3$ (8.1 mL, 72 mmol), and the mixture was stirred for 2 h at $-78\text{ }^\circ\text{C}$ under Ar. Then, the reaction mixture was allowed to warm to room temperature and evaporated to dryness. The residue was chromatographed on silica gel with $\text{CHCl}_3/\text{MeOH}$ (98/2) as an eluent, where the second fraction was collected and evaporated to leave boronic acid **8** as colorless transparent oil (4.8 g, 53%): ^1H NMR (CDCl_3) δ 7.80–7.70 (m, 4H, C_6H_5), 7.59 (d, 1H, C_6H_4), 7.50 (d, 1H, C_6H_4), 7.45–7.36 (m, 6H, C_6H_5), 7.21 (t, 1H, C_6H_4), 6.96 (d x 2, 1H, C_6H_4), 1.16 (s, 9H, *t*-Bu).

2-2. Synthesis of triaryl substituted porphyrin zinc complex **2**



Scheme 2. Reagents and conditions: (i) I₂, AgPF₆, CHCl₃/pyridine, r.t.; (ii) **8**, Pd(PPh₃)₄, K₂CO₃, DMF, 60 °C.

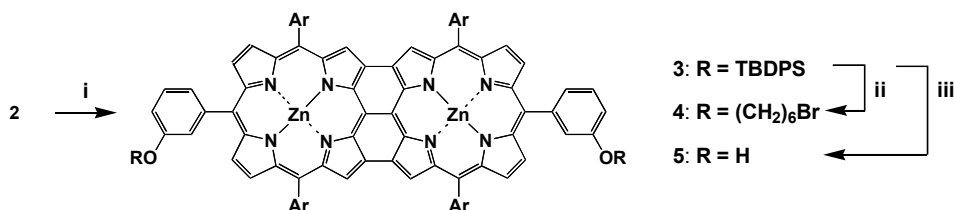
2: To a CHCl₃/pyridine (60/1) solution (66 mL) of **9** (499 mg, 0.67 mmol) (M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2405.) were added I₂ (168 mg, 0.66 mmol) and AgPF₆ (170 mg, 0.67 mmol), and the mixture was stirred for 30 min at room temperature. Then, the reaction mixture was washed with saturated aqueous KI and water, dried over Na₂SO₄ and evaporated to dryness. To a CHCl₃ solution (60 mL) of the residue was added 12 N aqueous HCl/MeOH (1/1, 5 mL), and the mixture, stirred for 10 min at room temperature, was treated with aqueous NaHCO₃, dried over Na₂SO₄ and evaporated to dryness. To a CHCl₃ solution (60 mL) of the residue was added a MeOH suspension of Zn(OAc)₂ (3 mL), and the mixture was stirred for 12 h at room temperature. Then, the reaction mixture was washed with water, dried over Na₂SO₄ and evaporated to dryness. The residue was chromatographed on silica gel with CHCl₃/hexane (1/2) as an eluent, where the first fraction containing **10** was collected and evaporated to dryness. To the residue (330 mg) dissolved in DMF (30 mL) were successively added boronic acid **8** (1.38 g, 3.6 mmol) and K₂CO₃ (495 mg, 3.6 mmol), and the mixture was subjected to freeze-pump-thaw cycles. To the resulting suspension was added Pd(PPh₃)₄ (87 mg, 0.33 mmol) under Ar, and the mixture was stirred for 3 h at 60 °C and evaporated to dryness under reduced pressure. Then, the residue was dissolved in AcOEt, and the solution was washed with water, dried over Na₂SO₄ and evaporated to dryness to give a crude product, which was subjected to recycling preparative size exclusion chromatography (SEC) with CHCl₃ as an eluent. The second fraction was collected and evaporated to leave **2** as purple solid (302 mg, 42%): ¹H NMR (CDCl₃) δ 10.23 (s, 1H, meso-H), 9.38 (d, 2H, pyrrole-β-H), 9.12 (d, 2H, pyrrole-β-H), 8.94 (d, 2H, pyrrole-β-H), 8.73 (d, 2H, pyrrole-β-H), 8.09 (t, 4H, Ar), 7.83–7.80 (m, 6H, Ar), 7.67–7.63 (m, 2H, Ar), 7.40–7.34 (m, 6H, Ar), 7.20–7.16 (m, 2H, Ar), 1.56 (s, 18H, *t*-Bu), 1.54 (s, 18H, *t*-Bu), 1.14 (s, 9H, *t*-Bu); MALDI-TOF-MS *m/z* calcd. for C₇₀H₇₄N₄OSiZn (M⁺) 1080.8, found

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1080.5.

2-3. Synthesis of fused porphyrin zinc complexes 3–5



Scheme 3. Reagents and conditions: (i) DDQ, Sc(OTf)₃, toluene, r.t.; (ii) Br(CH₂)₆Br, KF, 18-crown-6, acetone, 50 °C; (iii) TBAF, THF, r.t..

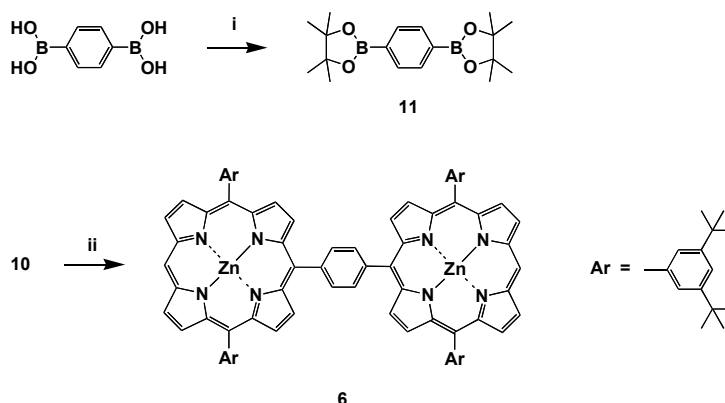
3: To a toluene solution (75 mL) of triarylporphyrin **2** (302 mg, 0.28 mmol), after freeze-pump-thaw cycles, was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (190 mg, 0.84 mmol), and the mixture was stirred for 10 min at room temperature. Then, Sc(OTf)₃ (412 mg, 0.84 mmol) was added, and the mixture was stirred for 15 h at room temperature. After the addition of THF (30 mL), followed by stirring for 1 h, the reaction mixture was washed with water, dried over Na₂SO₄ and evaporated to dryness. The residue was subjected to recycling preparative SEC with CHCl₃ as an eluent, where the first fraction was collected and evaporated to leave **3** as dark purple solid (205 mg, 63%): ¹H NMR (CDCl₃) δ 7.74 (t, 4H, Ar), 7.72 (d, 4H, pyrrole-β-H), 7.63 (d, 4H, pyrrole-β-H), 7.61 (t, 8H, Ar), 7.58 (d, 4H, Ar), 7.43 (d, 4H, Ar), 7.36–7.31 (m, 12H, Ar), 7.28 (s, 4H, pyrrole-β-H), 7.22–7.20 (m, 4H, Ar), 7.00–6.98 (m, 2H, Ar), 1.46 (s, 36H, *t*-Bu), 1.43 (s, 36H, *t*-Bu), 1.10 (s, 18H, *t*-Bu); MALDI-TOF-MS *m/z* calcd. for C₁₄₀H₁₄₂N₈O₂Si₂Zn₂ (M⁺) 2155.6, found 2155.4; UV-vis (toluene): λ_{max} (log ε) 420 (5.13), 461 (4.68), 585 (5.08), 927 (4.24), 1058 (4.50) nm.

4: An acetone suspension (8 mL) of a mixture of porphyrin **3** (82 mg, 0.04 mmol), 1,6-dibromohexane (2 mL, 13 mmol), KF (26 mg, 0.53 mmol) and 18-crown-6 (23 mg, 0.09 mmol) was stirred for 4 h at 50 °C under Ar and evaporated to dryness. The residue was chromatographed on silica gel with CH₂Cl₂ as an eluent, where the first fraction was collected and evaporated to dryness. A CHCl₃ solution (10 mL) of the residue was washed with water, dried over Na₂SO₄ and evaporated to dryness. The residue was subjected to recycling preparative SEC with CHCl₃ as an eluent, where the first fraction was collected and evaporated to leave **4** as dark purple solid (77 mg, 97%): ¹H NMR (CDCl₃) δ 7.72 (t, 4H, pyrrole-β-H), 7.66 (d, 4H, pyrrole-β-H), 7.63 (br, 8H, Ar), 7.60 (br, 4H, Ar), 7.45–7.36 (m, 6H, Ar), 7.32 (s, 4H, pyrrole-β-H), 7.10–7.07 (m, 2H, Ar), 4.02 (t, 4H, OCH₂), 3.38 (t, 4H, CH₂Br), 1.89–1.78 (m, 4H, OCH₂CH₂C₄H₈Br), 1.60–1.45 (m,

12H, OC₂H₄(CH₂)₃CH₂Br), 1.43 (s, 72H, *t*-Bu); MALDI-TOF-MS *m/z* calcd. for C₁₄₈H₁₇₆Br₂N₈O₁₈Zn₂ (M⁺) 2003.7, found 2004.1.

5: To a THF solution (10 mL) of **3** (115 mg, 0.053 mmol) was added a THF solution of *n*-Bu₄NF (TBAF; 1.0 M, 0.5 mL), and the mixture was stirred for 1 h at room temperature and evaporated to dryness. A CHCl₃ solution (10 mL) of the residue was washed with water, dried over Na₂SO₄ and evaporated to dryness. The residue was subjected to preparative SEC with toluene as an eluent, where the first fraction was collected and evaporated to dryness. The residue was recrystallized from CHCl₃/cyclohexane to leave **5** as black solid (85 mg, 95%): ¹H NMR (CDCl₃) δ 7.71 (d, 4H, pyrrole-β-H), 7.67 (d, 4H, pyrrole-β-H), 7.63 (t, 8H, Ar), 7.60 (t, 4H, Ar), 7.41–7.34 (m, 6H, Ar), 7.34 (s, 4H, pyrrole-β-H), 7.06–7.02 (m, 2H, Ar), 4.76 (s, 2H, OH), 1.43 (s, 72H, *t*-Bu); MALDI-TOF-MS *m/z* calcd. for C₁₀₈H₁₀₆N₈O₂Zn₂ (M⁺) 1678.8, found 1678.5.

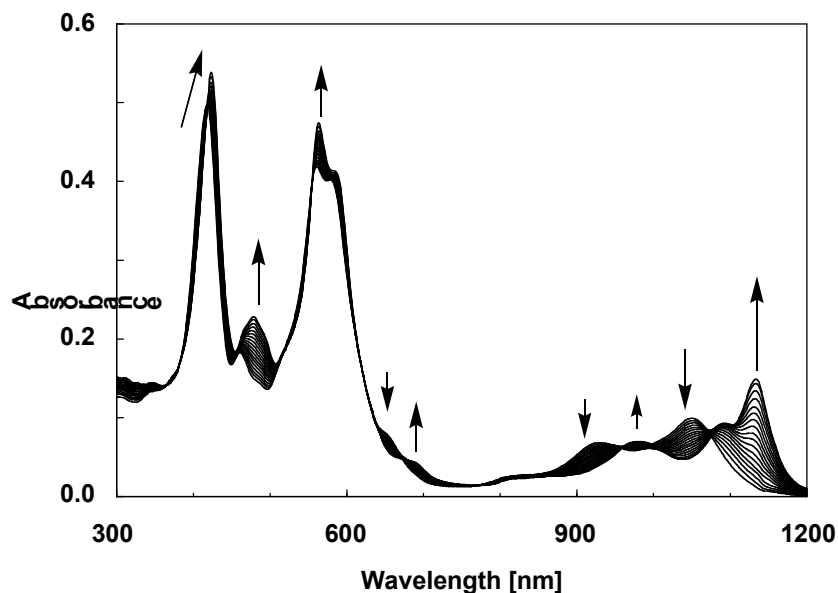
2-4. Synthesis of phenylene-bridged diporphyrin zinc complex **6**



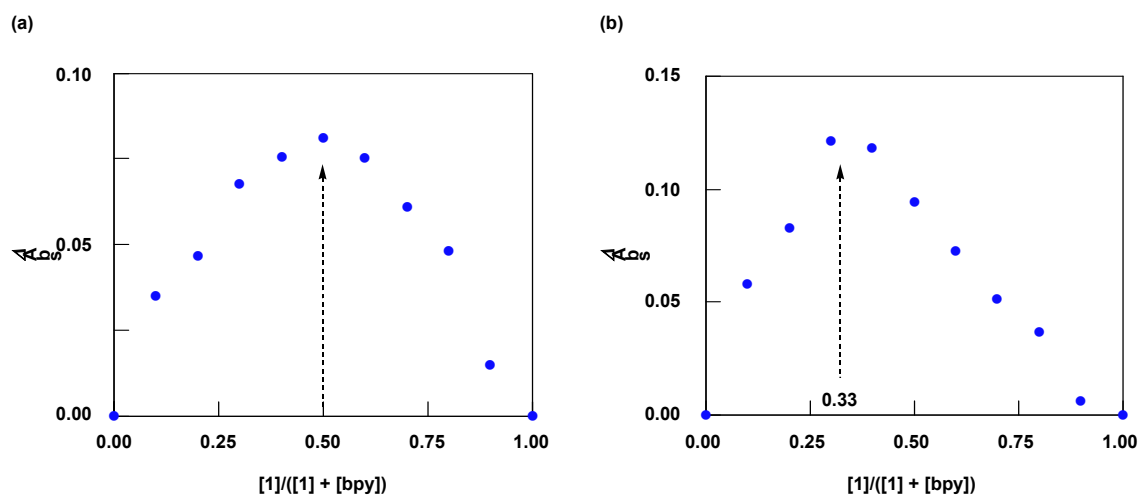
Scheme 4. Reagents and conditions: (i) pinacol, Et₂O, r.t., 1 d.; (ii) **11**, Pd(PPh₃)₄, K₂CO₃, DMF, 60 °C, 2 d..

6: An ether solution (10 mL) of a mixture of 1,4-phenylenediboronic acid (500 mg, 3.0 mmol) and pinacol (785 mg, 6.6 mmol) was stirred for 12 h at room temperature and evaporated to dryness. The residue dissolved in CHCl₃ was chromatographed on silica gel with CHCl₃ as an eluent, where the first fraction was collected and evaporated to leave **11** as white solid (940 mg, 95%). To a DMF solution (10 mL) of **11** (27 mg, 0.08 mmol) were added K₂CO₃ (184 mg, 3.6 mmol) and the solid substance containing **10** (70 mg; see preparation of compound **2**), and the mixture was subjected to freeze-pump-thaw cycles. Then, Pd(PPh₃)₄ (192 mg, 0.33 mmol) was added to the resulting suspension under Ar, and the mixture was stirred for 2 days at 60 °C and evaporated to dryness under reduced pressure. The residue was dissolved in AcOEt, and the solution was washed with water, dried over Na₂SO₄ and evaporated to dryness. The residue was subjected to preparative SEC with toluene as an eluent, where the third fraction was collected and evaporated to leave **6** as purple solid (59 mg, 32%): ¹H NMR (CDCl₃) δ 10.31 (s, 2H, meso-H), 9.45 (d x 2, 8H, pyrrole-β-H), 9.21 (t, 8H, pyrrole-β-H), 8.61 (s, 4H, Ar), 8.19 (d, 8H, Ar), 7.85 (t, 4H, Ar), 1.58 (s, 72H, *t*-Bu); MALDI-TOF-MS *m/z* calcd. for C₇₀H₇₄N₄OSiZn (M⁺) 1080.8, found 1080.5; UV-vis (toluene): λ_{max} (log ε) 419 (5.66), 426 (5.68), 546 (4.55) nm.

3. Spectroscopic titration of cyclic host **1** with 4,4'-bipyridine (bpy) in toluene at 20 °C. $[1]_0 = 1.6 \times 10^{-6}$ M; $[bpy]/[1] = 0-2.0$

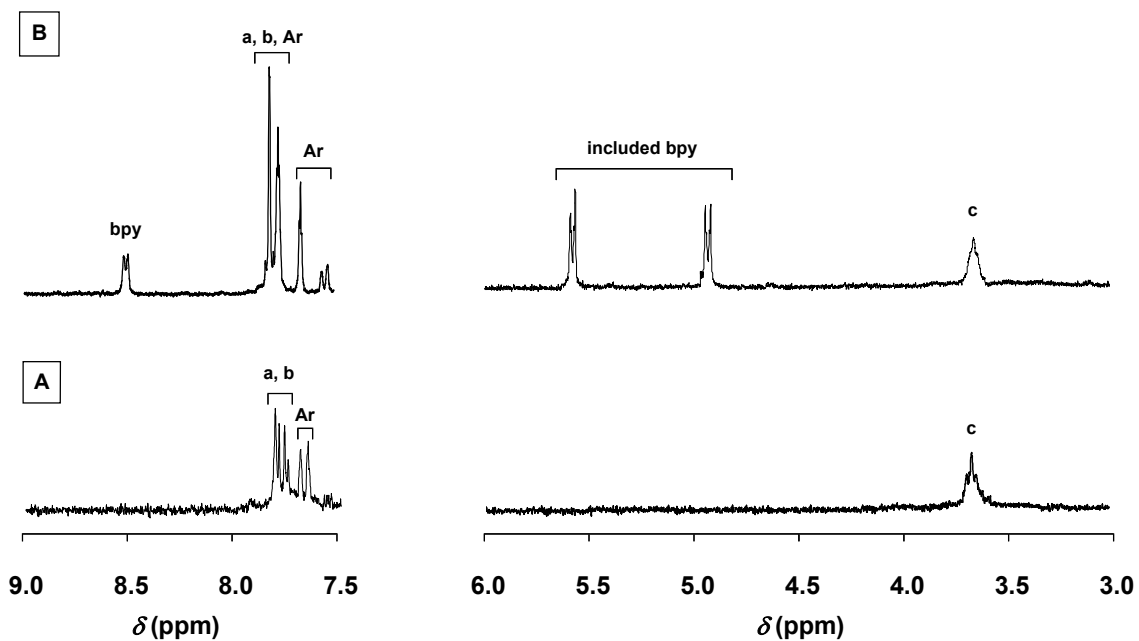
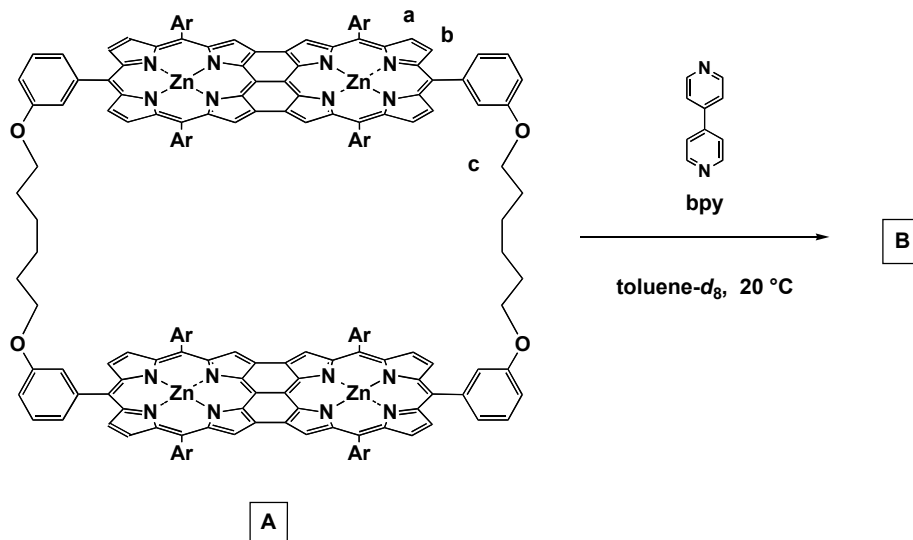


4. Job's plots (Δ Abs; monitored at (a) 1107 and (b) 1122 nm) upon mixing of cyclic host **1** with 4,4'-bipyridine (bpy) in toluene at 20 °C. $[1] + [bpy] = 5.9 \times 10^{-6}$ M

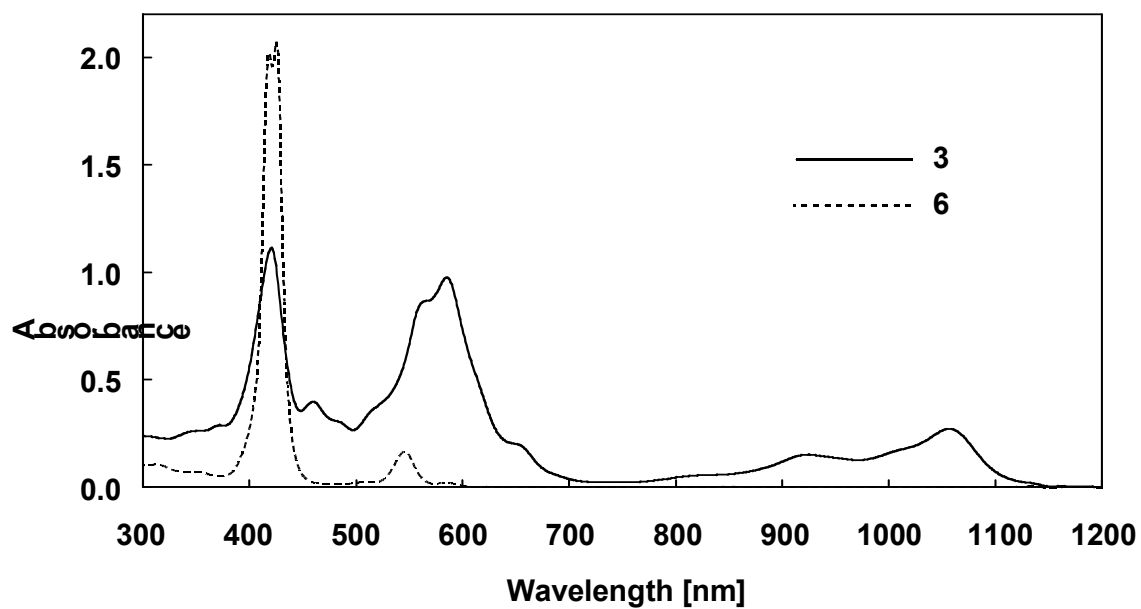


The formation of **1**⊃bpy (a) and **1**⊃bpy₂ (b) was confirmed by appropriate selection of the monitoring wavelengths sensitive to the 1:1 and 1:2 complexations, respectively.

5. ^1H NMR spectra (pyrrole- β , Ar and OCH_2 proton regions) of cyclic host 1 (A) and 1:bpy₂ (1:2.5) (B) in toluene-*d*₈ at 20 °C

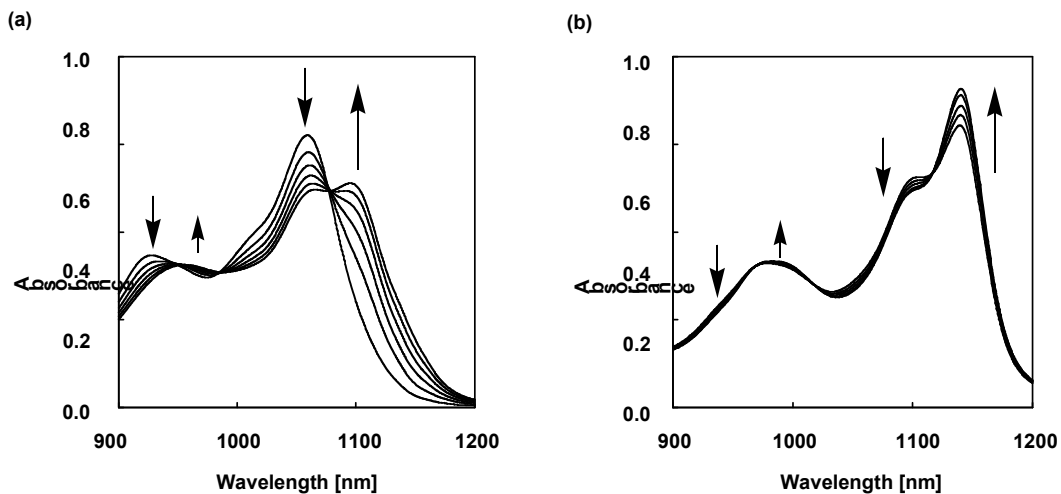


6. Absorption spectra of the zinc complexes of fused porphyrin 3 and phenylene-bridged diporphyrin 6 in toluene at 20 °C. [3] and [6] = 8.6×10^{-6} M



7. Spectroscopic titration of the zinc complexes of fused porphyrin **3** and phenylene-bridged diporphyrin **6** with pyridine (py) in toluene at 20 °C

7-1. $[3]_0 = 2.5 \times 10^{-5}$ M; (a) $[py]/[3] = 0-5$ and (b) 50-90



7-2. $[6]_0 = 1.5 \times 10^{-6}$ M; (a) $[py]/[6] = 0-24$ and (b) 27-78

