

Supplementary data

**Reversible caterpillar-motion-like isomerization in a *N,N'*-dimethyl
hexaphyrin(1.1.1.1.1) induced by two-electron oxidation or reduction**

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1. Compound Data

• 15,30-bis(2,4,6-trifluorophenyl)-5,10,20,25-tetrakis(pentafluorophenyl)[26]hexaphyrin 3

¹H NMR (600 MHz, CDCl₃): δ = -2.55 (s, 4H, inner βCH), -2.16 (br, NH), 7.80 (m, 4H, phenyl), 9.15 (d, *J* 4.6 Hz, 4H, outer βCH), and 9.41 (d, *J* 4.4 Hz, 4H, outer βCH) ppm; UV/Vis(CH₂Cl₂): λ_{max} = 1022, 894, 772, 715, and 568 nm; ESI-TOF-MS (positive-mode) (%intensity) : C₆₆H₁₉F₂₆N₆ [M+H]: calcd.: 1389.13, found : 1389.11 (100).

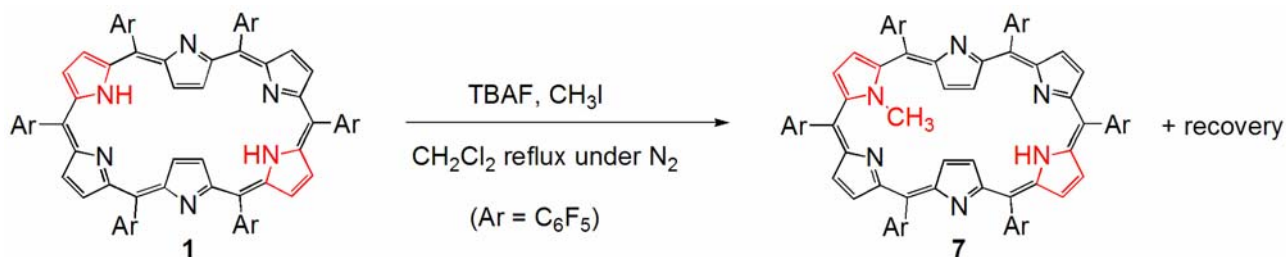
• 5,20-bis(2,4,6-trifluorophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin 4

4 was not obtained as a pure form. ¹H NMR (600 MHz, CDCl₃): δ = -2.60 (d, *J* 4.1 Hz, 2H, inner βCH), -2.54 (d, *J* 3.8 Hz, 2H, inner βCH), -2.16 (br, NH), 7.20-7.90 (phenyl), 9.08 (d, *J* 4.6 Hz, 2H, outer βCH), 9.11 (d, *J* 5.0 Hz, 2H, outer βCH), 9.42 (not clear, outer βCH), and 9.52 (d, *J* 4.6 Hz, 2H, outer βCH) ppm.

• 5,20-bis(2,4,6-trifluorophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[28]hexaphyrin 6

¹H NMR (600 MHz, CDCl₃): δ = 2.31 (s, 2H, inner βCH), 2.44 (s, 2H, inner βCH), 3.98 (s, 2H, outer NH), 6.71 (t, *J* 7.8 Hz, phenyl), 7.65 (d, *J* 4.6 Hz, 2H, outer βCH), 7.68 (d, *J* 5.0 Hz, 2H, outer βCH), 7.70 (d, *J* 4.6 Hz, 2H, outer βCH), and 7.80 (d, *J* 4.6 Hz, 2H, outer βCH) ppm; UV/Vis(CH₂Cl₂): λ_{max} = 763, 591, 445, and 389 nm; ESI-TOF-MS (positive-mode) (%intensity) : C₆₆H₁₉F₂₆N₆ [M+H]: calcd. : 1391.14, found : 1391.17 (100).

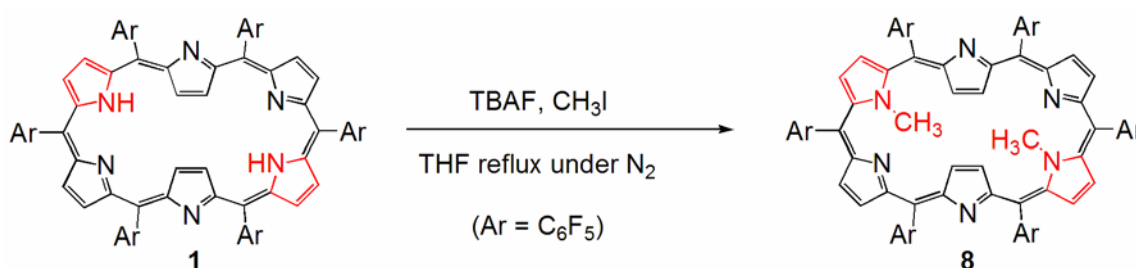
• meso-pentafluorophenyl N-methyl[26]hexaphyrin 7



Hexaphyrin **1** (50 mg, 0.0342 mmol) was added to a solution of TBAF·3H₂O (100 mg, large excess) and CH₃I (11 μl, 0.171 mmol) in CH₂Cl₂ (22 ml) and the resulting mixture was refluxed overnight. The solution was washed with water and evaporated. The reaction mixture was separated by silica gel

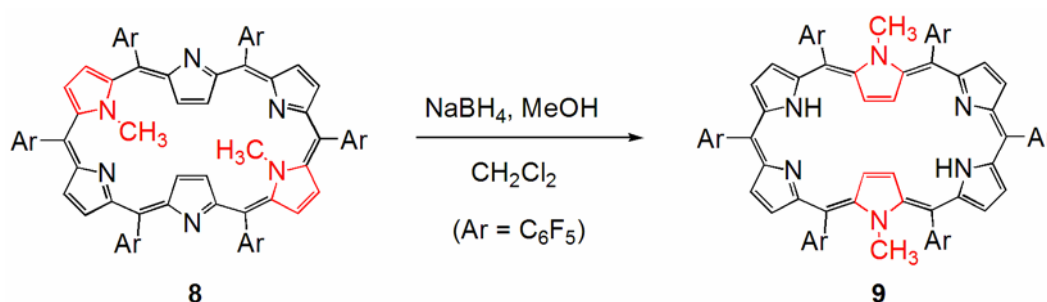
column chromatography with a 1:1 mixture of CH₂Cl₂ and hexane as an eluent. After recrystallization from a mixture of CH₂Cl₂ and hexane, *N*-methyl hexaphyrin **7** was obtained as green solids (21.5 mg, 43 %) together with the recovery of **1** (19 mg, 38%). ¹H NMR (600 MHz, CDCl₃): δ = -3.31 (s, 3H, methyl), -1.70 (d, *J* 4.1 Hz, 1H, inner βCH), -1.08 (d, *J* 4.1 Hz, 1H, inner βCH), -0.96 (d, *J* 4.5 Hz, 1H, inner βCH), -0.78 (br, NH), -0.61 (d, *J* 4.5 Hz, 1H, inner βCH), 7.80 (d, *J* 4.6 Hz, 1H, outer βCH), 8.15 (d, *J* 4.6 Hz, 1H, outer βCH), 8.62 (d, *J* 4.8 Hz, 1H, outer βCH), 8.71 (d, *J* 4.8 Hz, 1H, outer βCH), 8.72 (d, *J* 4.8 Hz, 1H, outer βCH), 8.77 (d, *J* 4.8 Hz, 1H, outer βCH), 9.06 (d, *J* 4.8 Hz, 1H, outer βCH), and 9.14 (d, *J* 4.8 Hz, 1H, outer βCH) ppm; UV/Vis(CH₂Cl₂): λ_{max}(ε) = 1041 (1800), 896 (4100), 774 (11000), 717 (19000), 570 (190000), and 406 (23000) nm; ESI-TOF-MS (positive-mode) (%intensity) : C₆₇H₁₇F₃₀N₆ [M+H]: calcd. : 1475.1030, found : 1475.0851 (100).

• *meso*-pentafluorophenyl *N,N'*-dimethyl [26]hexaphyrin **8**



A solution of TBAF in THF (10 mM, 11 ml, 0.00684 mmol) was added into a solution of **1** (50 mg 0.0342 mmol) and CH₃I (2 ml, large excess) in THF (60ml) and the resulting mixture was refluxed for 1 day under nitrogen. The solution was washed with water and evaporated. The reaction mixture was separated by silica gel column chromatography with a 1:1 mixture of CH₂Cl₂ and hexane to give *N,N'*-dimethyl hexaphyrin **8** as green solids (24 mg, 50 %). ¹H NMR (600 MHz, CDCl₃): δ = -2.93 (s, 6H, methyl), -0.95 (s, 2H, inner βCH), -0.07 (s, 2H, inner βCH), 7.68 (s, 2H, outer βCH), 8.03 (s, 2H, outer βCH), 8.38 (s, 2H, outer βCH), and 8.57 (s, 2H, outer βCH) ppm; UV/Vis(CH₂Cl₂): λ_{max}(ε [M⁻¹cm⁻¹]) = 919 (1900), 872 (1600), 787 (12000), 722 (14000), 578 (160000), and 406 (22000) nm; ESI-TOF-MS (positive-mode) (%intensity) : C₆₈H₁₉F₃₀N₆ [M+H]: calcd. : 1489.1197, found : 1489.1170 (100).

• *N,N'*-dimethyl [28]hexaphyrin **9**



N,N'-Dimethyl [26]hexaphyrin **8** was dissolved in CH₂Cl₂, to which NaBH₄ and methanol were added carefully. The resulting mixture was stirred for 1 h and quenched with water. *N,N'*-Dimethyl [28]hexaphyrin **9** was obtained as green solids by recrystallization from a mixture of CH₂Cl₂ and

methanol. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ = 2.49 (s, 6H, methyl), 4.37 (s, 4H, inner βCH), 7.17 (s, 8H, outer βCH) and 7.48 (br, inner NH) ppm; UV/Vis(CH_2Cl_2): $\lambda_{\text{max}}(\epsilon [\text{M}^{-1}\text{cm}^{-1}])$ = 769 (9800), 606 (140000), and 434 (32000) nm.; ESI-TOF-MS (negative-mode) (%intensity) : $\text{C}_{68}\text{H}_{19}\text{F}_{30}\text{N}_6$ [$\text{M}-\text{H}$]: calcd.: 1489.1198, found : 1489.0729 (100).

• *meso*-hexakis(pentafluorophenyl) [26]hexaphyrin dianion

Dianion of **1** was prepared by addition of excess amounts of TBAF or TBAT. $^1\text{H NMR}$ (600 MHz, CDCl_3): δ = -4.33 (s, 4H, inner βCH), 9.21(s, 4H, outer βCH) and 9.51 (s, 4H, outer βCH) ppm; UV/Vis(CH_2Cl_2): $\lambda_{\text{max}}(\epsilon)$ = 975 (16000), 880 (22000), 823 (20000), 617 (370000), and 601 (570000) nm.

2. $^1\text{H-NMR}$ Spectra.

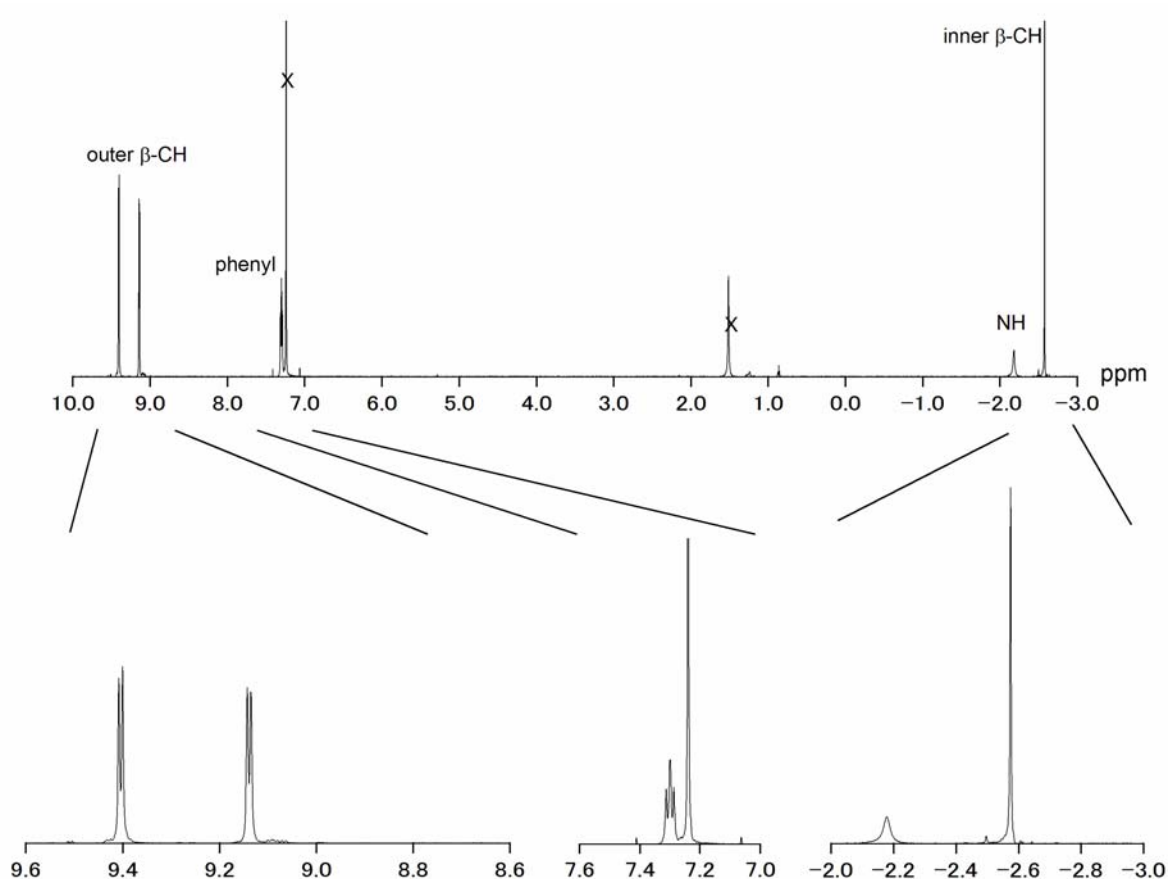


Fig. S1 $^1\text{H NMR}$ spectrum of **3** in CDCl_3 .

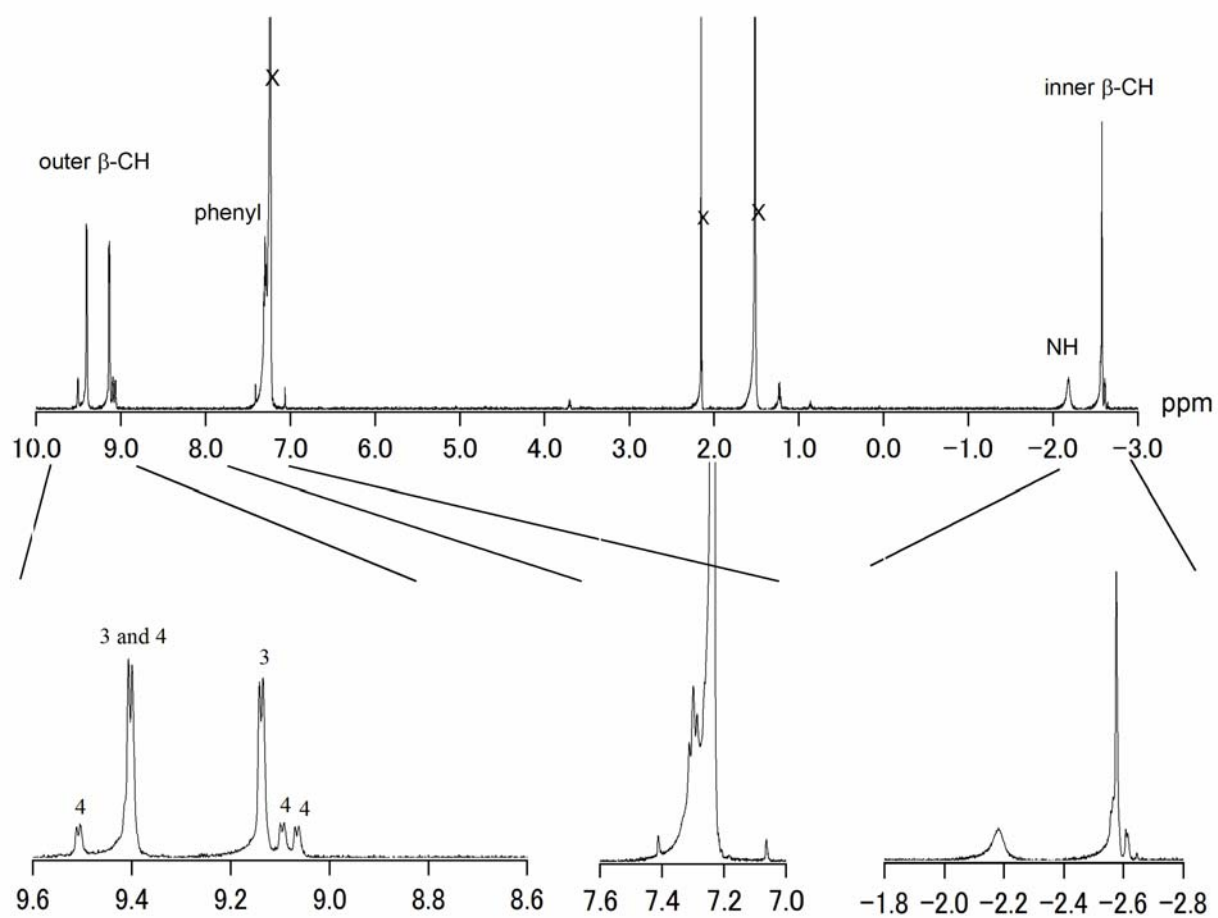


Fig. S2 ^1H NMR spectrum of 3 and 4 in equilibrium state in CDCl_3 .

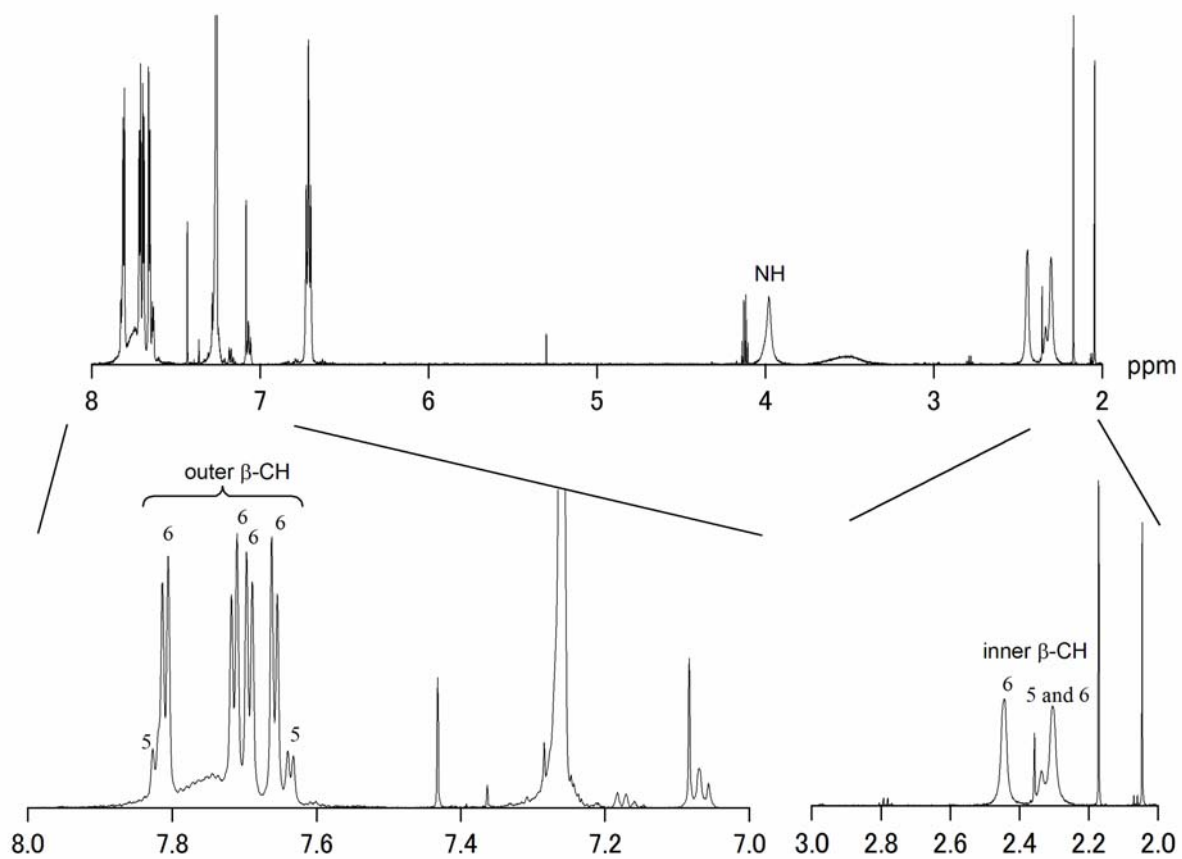


Fig. S3 ^1H NMR spectrum of **5** and **6** in equilibrium state in CDCl_3 . The ethyl quartet at 4.12 ppm was due to contaminated ethyl acetate

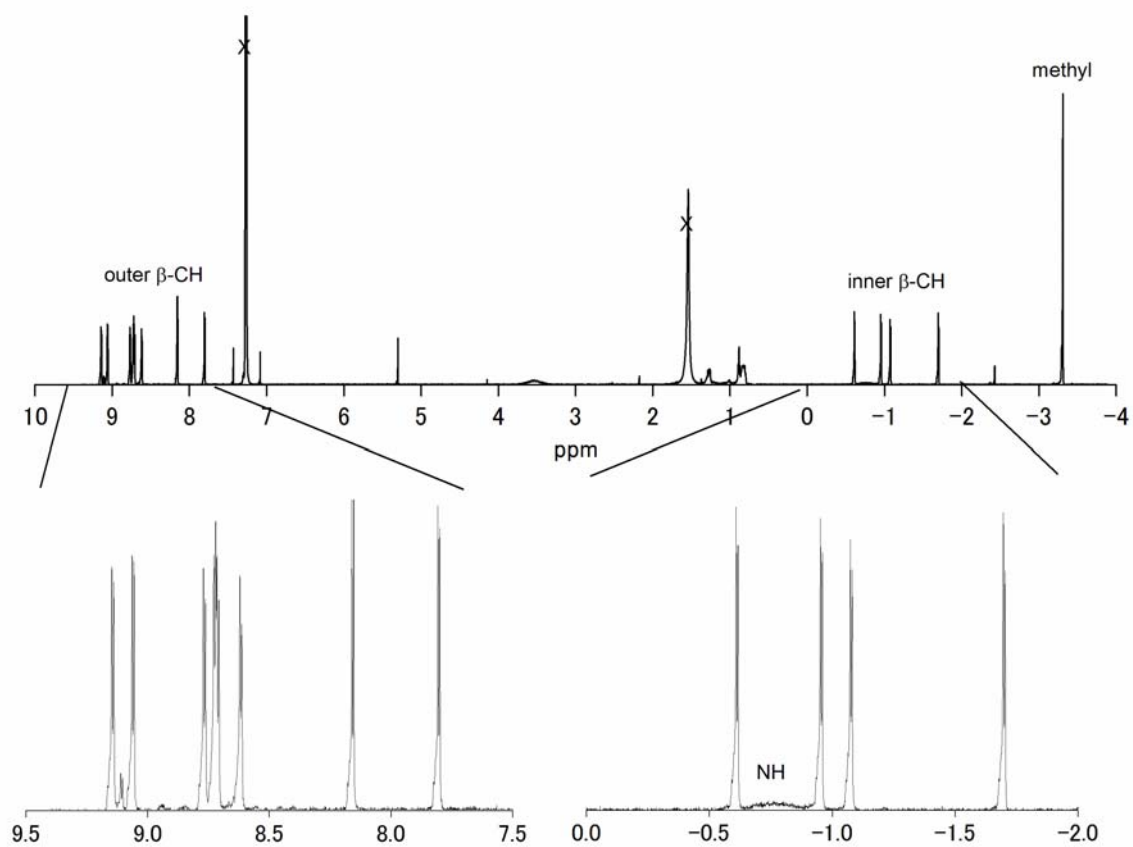


Fig. S4 ^1H NMR spectrum of **7** in CDCl_3 .

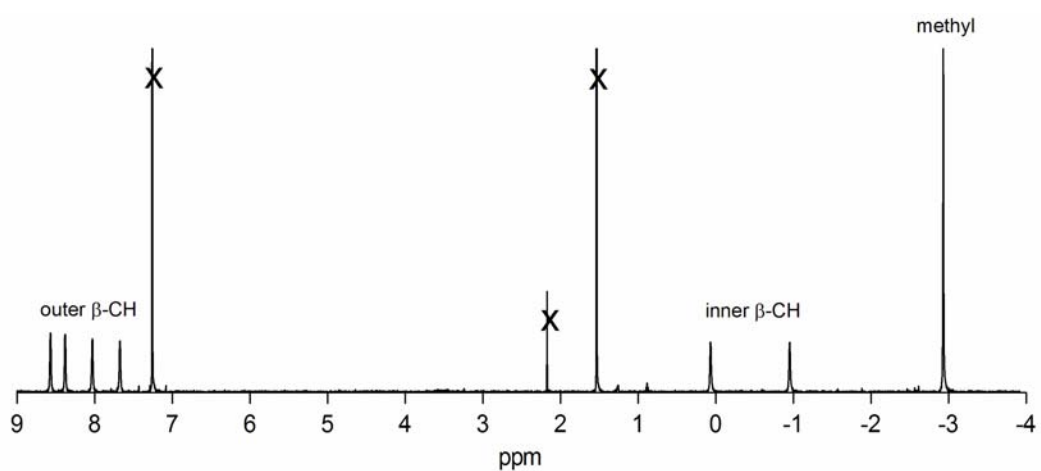


Fig. S5 ^1H NMR spectrum of **8** in CDCl_3 .

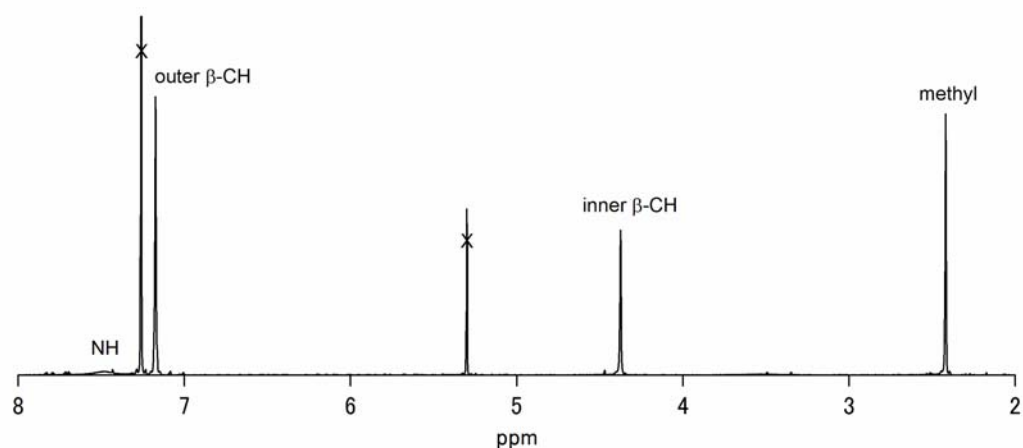


Fig. S6 ^1H NMR spectrum of **9** in CDCl_3 .

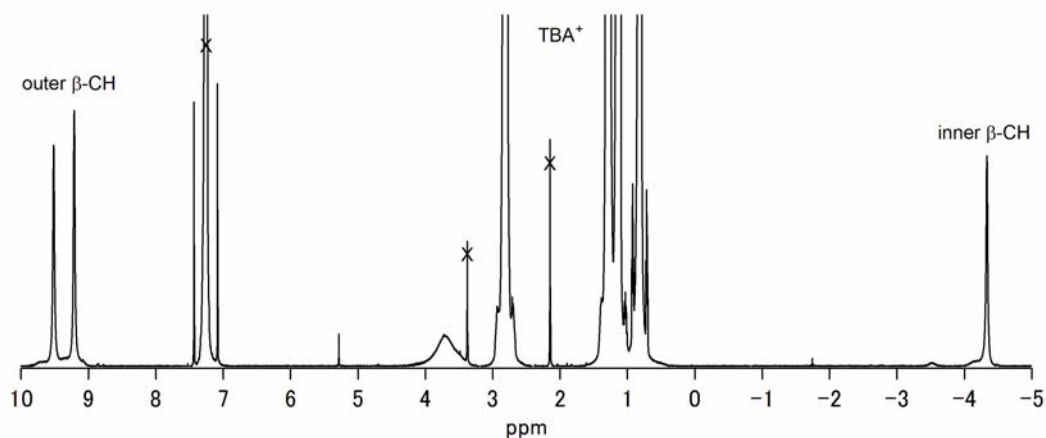


Fig. S7 ^1H NMR spectrum of dianion of **1** in CDCl_3 .

3. UV-visible Absorption Spectra.

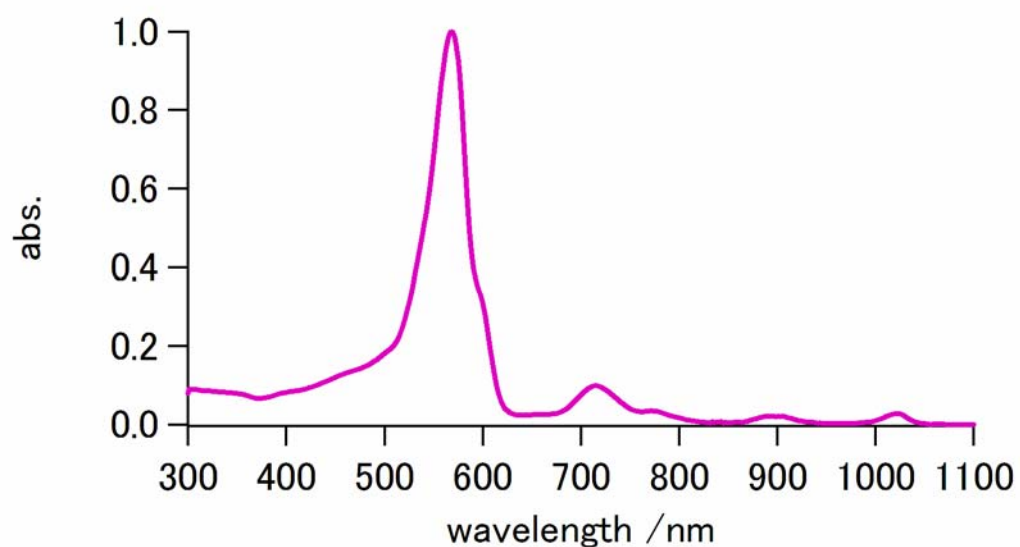


Fig. S8 UV/visible absorption spectrum of **3** in CH_2Cl_2 .

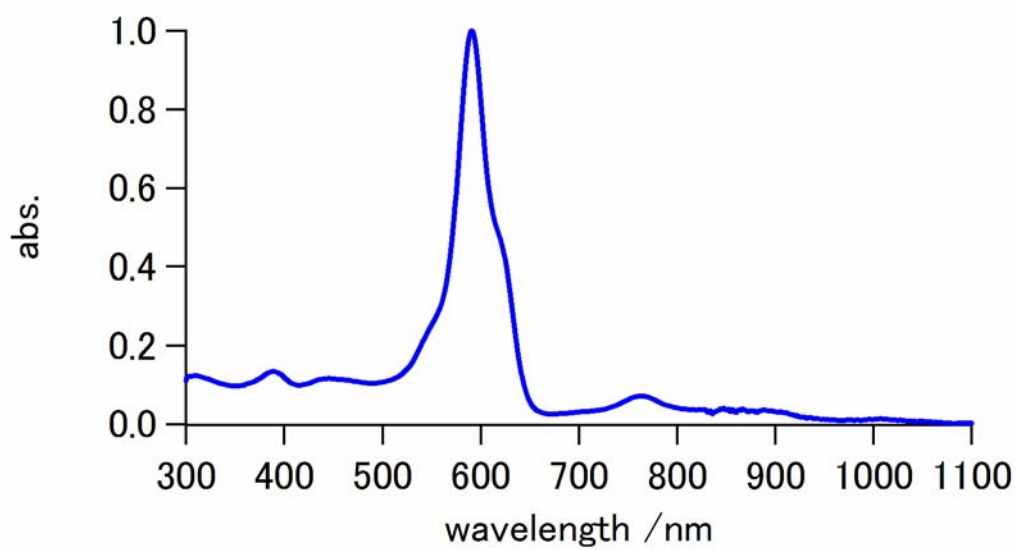


Fig. S9 UV/visible absorption spectrum of 5 in CH₂Cl₂.

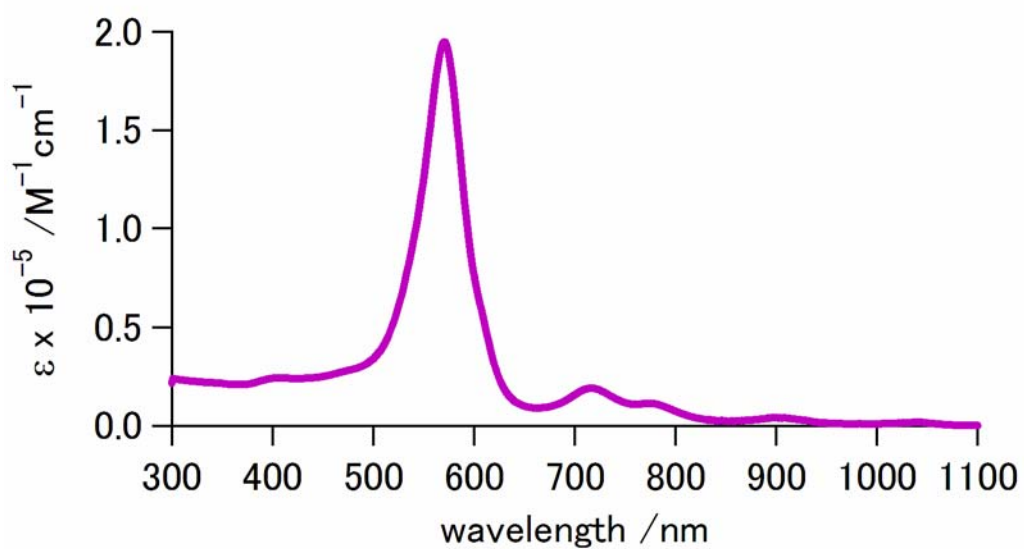


Fig. S10 UV/visible absorption spectrum of 7 in CH₂Cl₂.

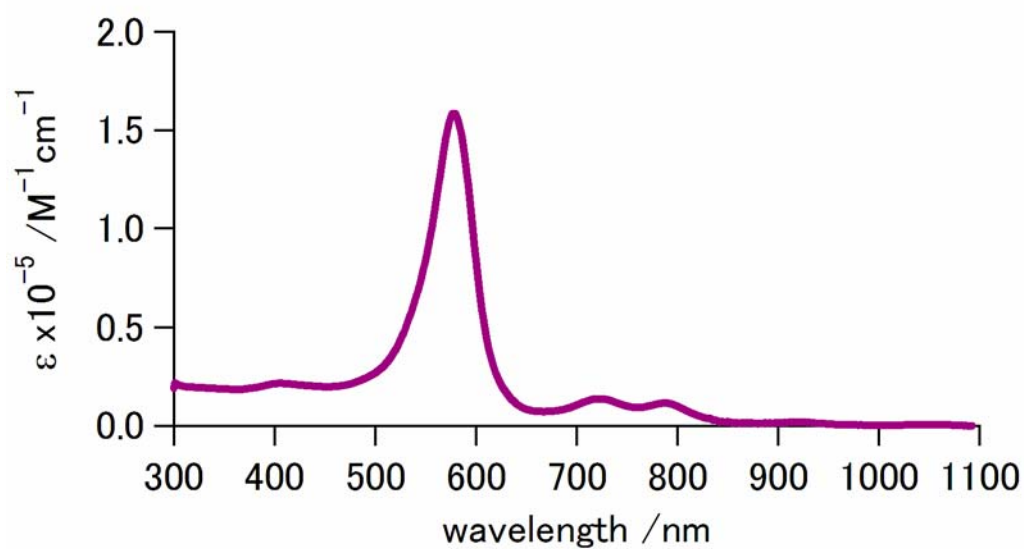


Fig. S11 UV/visible absorption spectrum of 8 in CH₂Cl₂.

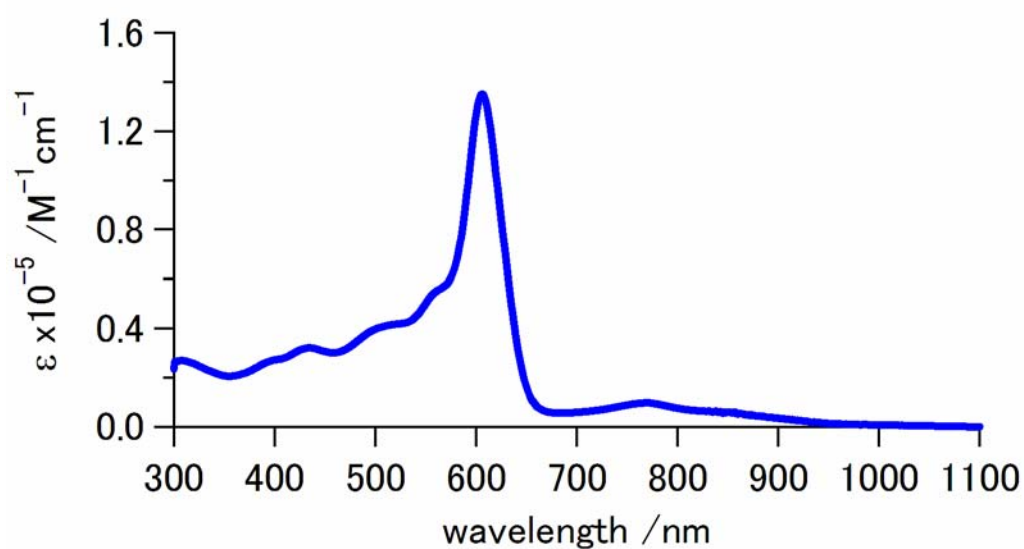


Fig. 12 UV/visible absorption spectrum of 9 in CH₂Cl₂.

4. ESI-TOF Mass Spectra.

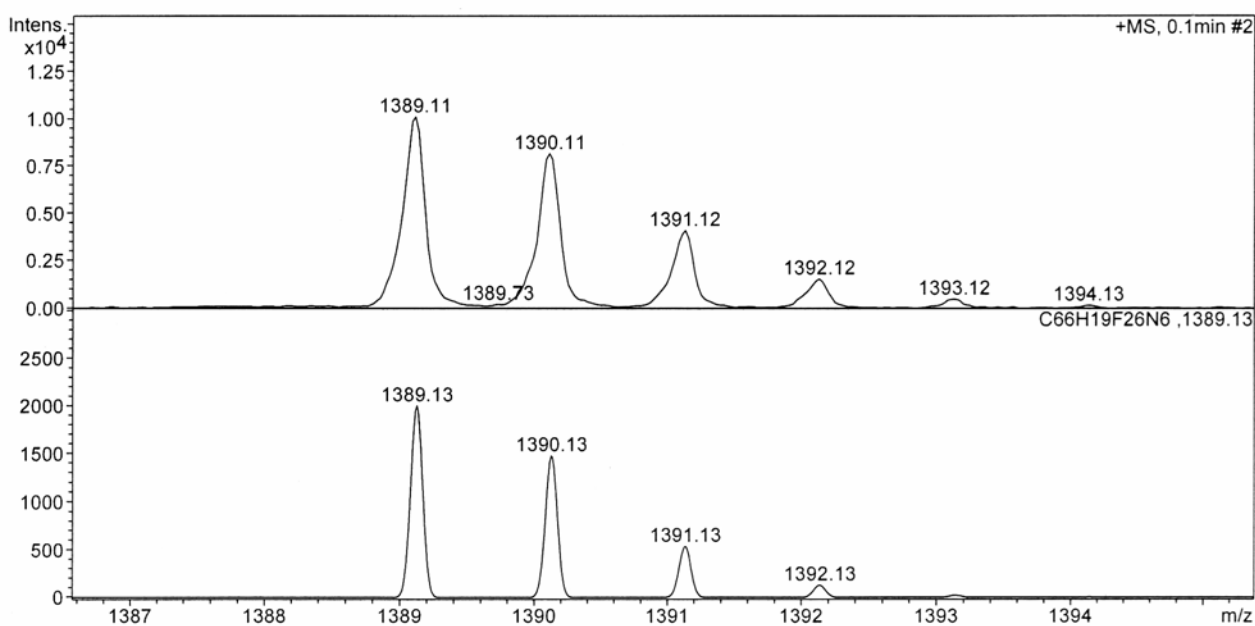


Fig. S13 ESI-TOF mass spectrum of 3 (4). Upper: observed; lower: calculated.

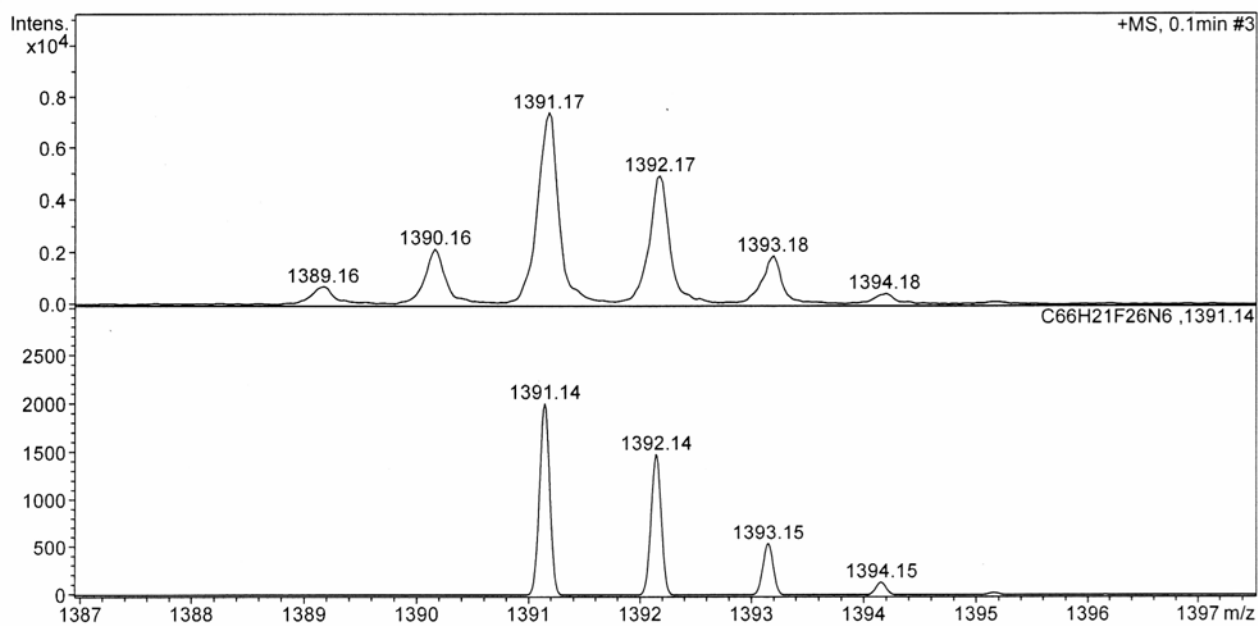


Fig. S14 ESI-TOF mass spectrum of 5 (6). Upper: observed; lower: calculated.

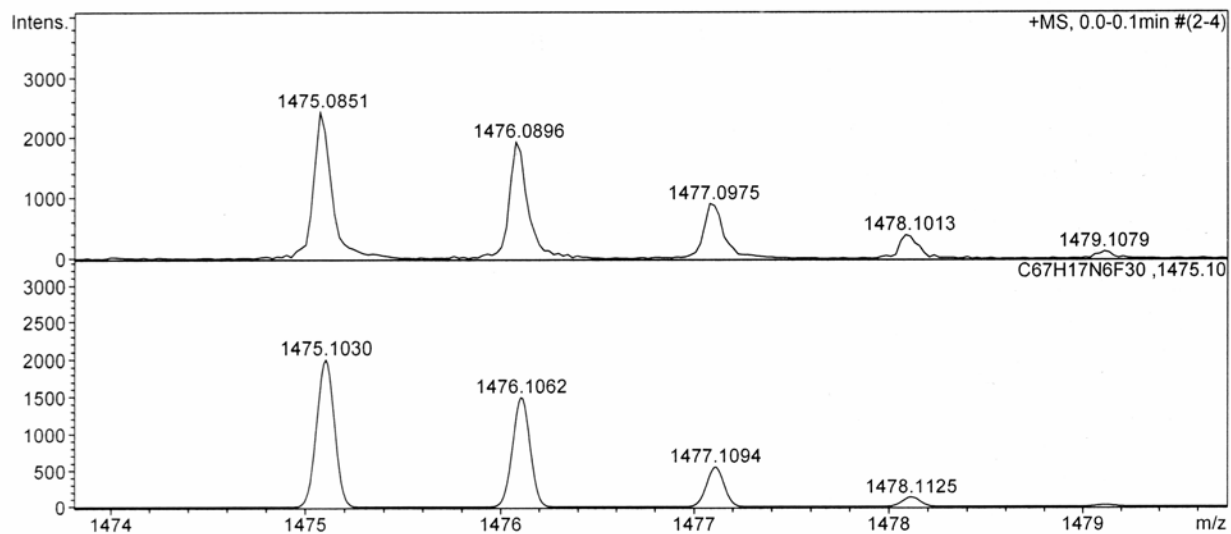


Fig. S15 ESI-TOF mass spectrum of **7**. Upper: observed; lower: calculated.

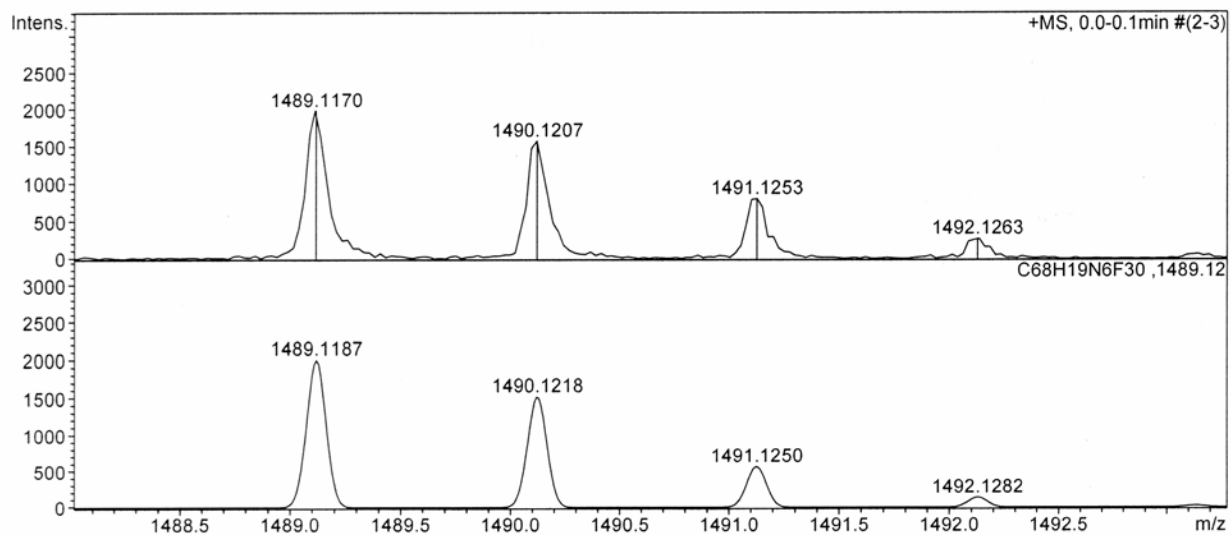


Fig. S16 ESI-TOF mass spectrum of **8**. Upper: observed; lower: calculated.

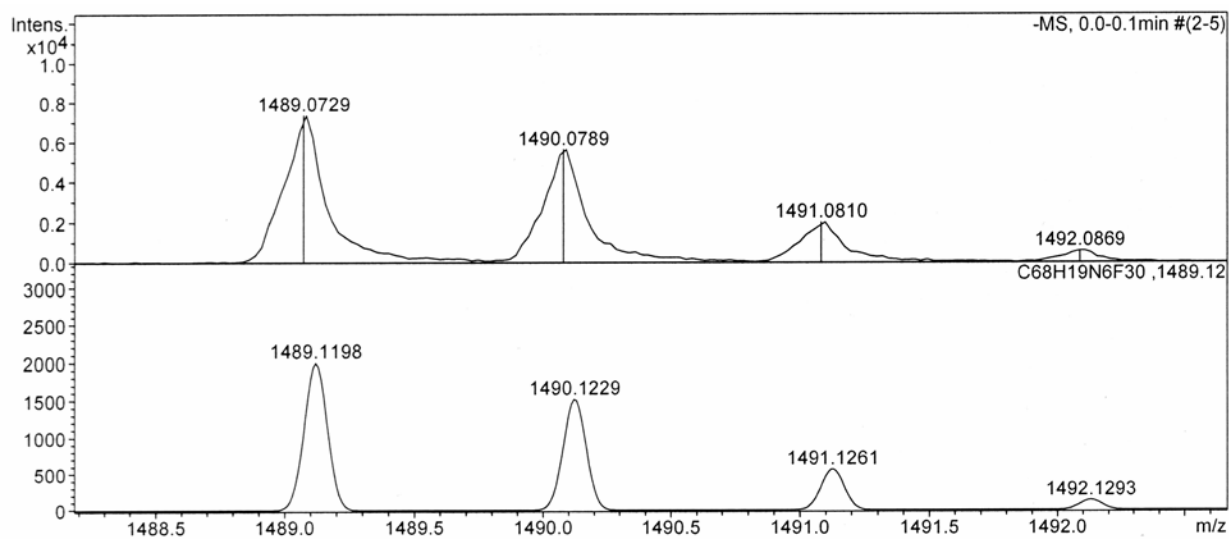


Fig. S17 ESI-TOF mass spectrum of 9. Upper: observed; lower: calculated.

5. Determination of the activation barrier for isomerization.

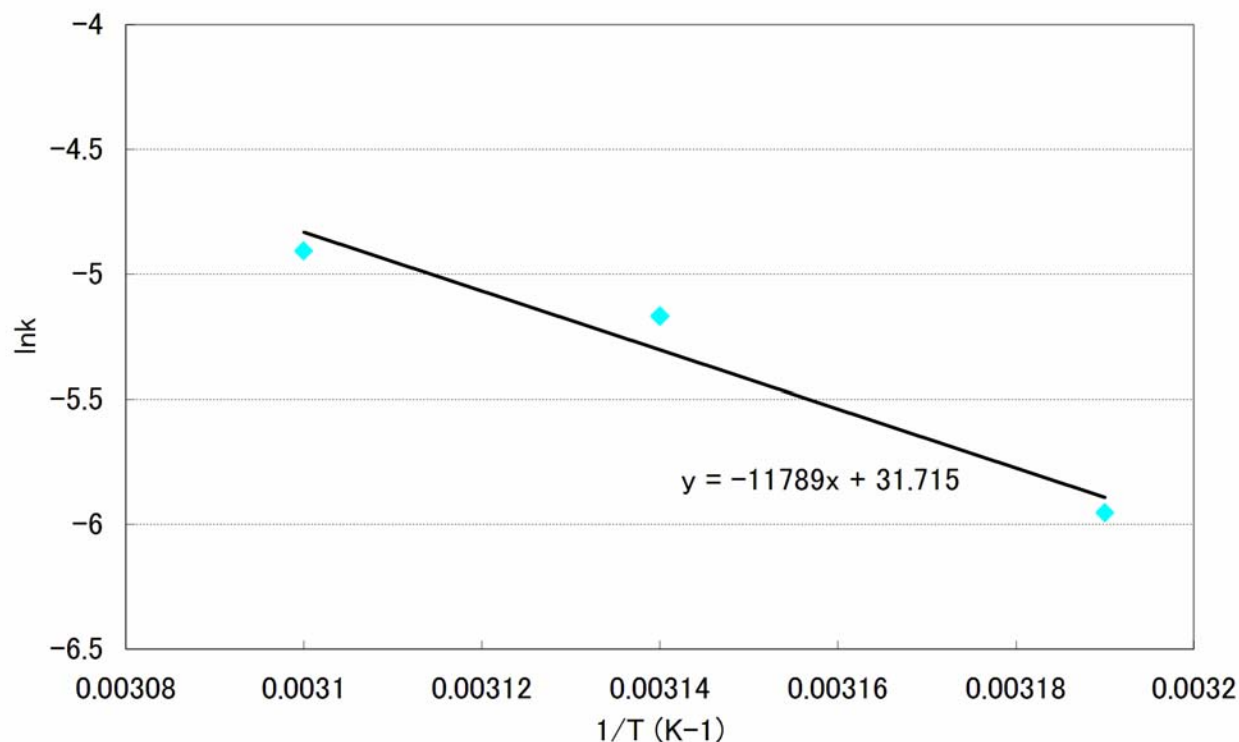


Fig. S18 Arrhenius plot of isomerization between 3 and 4. Activation energy value (E_a) was calculated by the following formula.

$$-E_a/R = -11789$$
$$E_a = 11789/8.3 = 1420 \text{ [J/mol]} = 1.42 \text{ [KJ/mol]}$$

6. Mean Plane Deviation Diagrams.

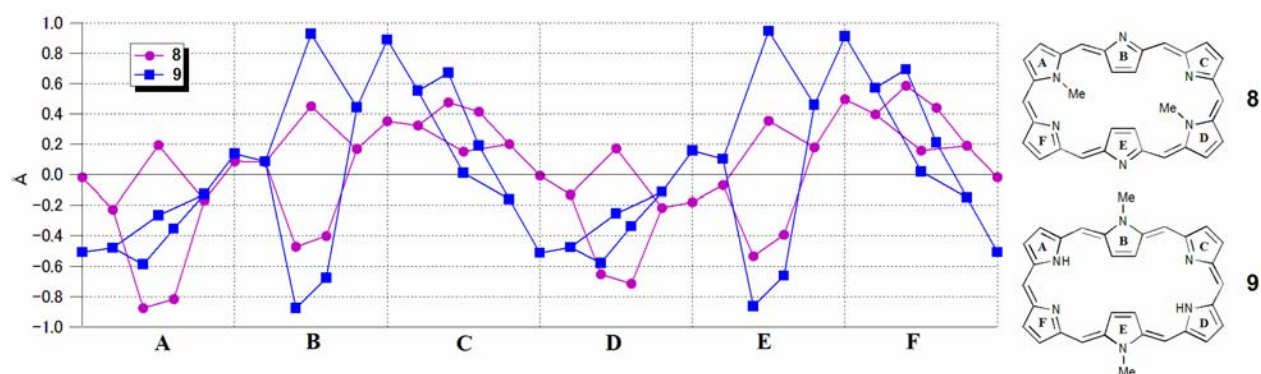


Fig. S19 Comparison of mean plane deviation diagrams of 8 and 9.

7. Structural comparison of 1 and its dianion.

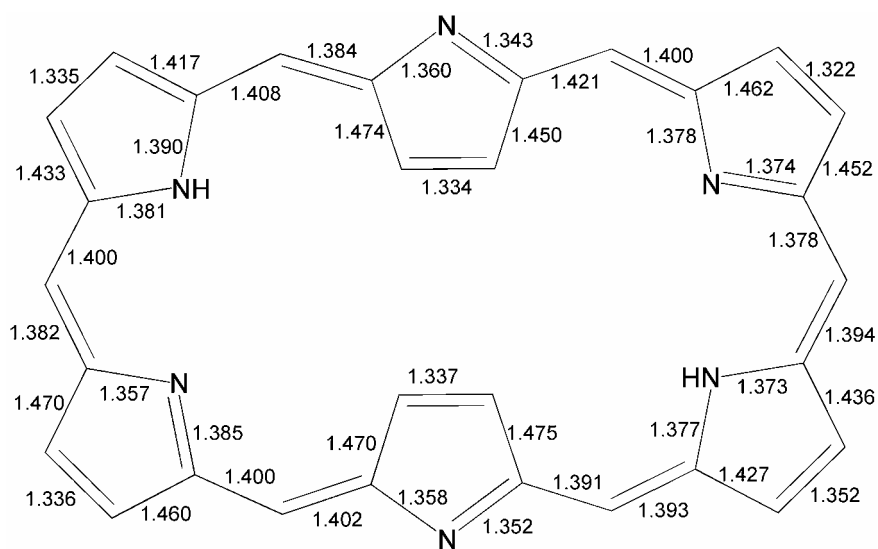


Fig. S20 Structure of 1.

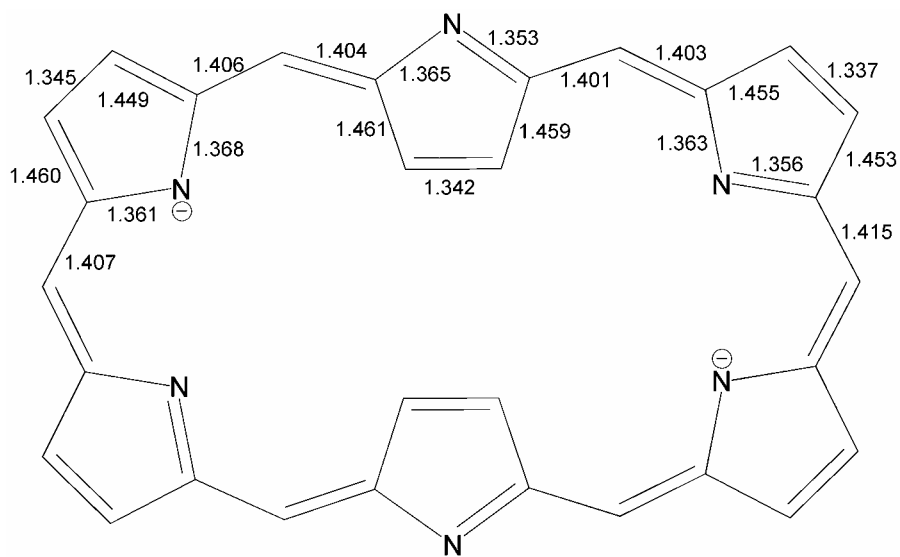


Fig. S21 Structure of dianion of **1**.