



Supporting Information

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Boron(III) Subporphyrin Extrusion from *meso*-Heptakis(pentafluorophenyl) [32]Heptaphyrin upon Cooperative Cu^{II} and B^{III} Metallation

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Experimental Section

General Information

Dichloromethane and ethyldiisopropylamine (EDIPA) for reactions were distilled over CaH₂. All reagents were of the commercial reagent grade and were used without further purification except where noted. Silica gel column chromatography was performed on Wakogel C-300. UV-visible spectra were recorded on a Shimadzu UV-3100PC spectrometer. ¹H (600.17 MHz), ¹¹B (192.56 MHz), ¹³C (150.91 MHz) and ¹⁹F NMR (564.73MHz) spectra were recorded on a JEOL ECA-600 spectrometer. Chemical shifts were reported as the delta scale in ppm relative to the residual solvent as the internal reference for ¹H (δ = 7.26 ppm in CDCl₃) and ¹³C (δ = 77.0 ppm in CDCl₃). Boron trifluoride diethyl etherate for ¹¹B (δ = 0.0 ppm) and hexafluorobenzene for ¹⁹F (δ = -162.9 ppm) were employed as external references. Mass spectra were recorded on a BRUKER microTOF model using positive mode ESI-TOF method for acetonitrile solutions of samples, or on Shimadzu KRATOS KOMPACT MALDI4 using positive-MALDI-TOF method. Fluorescence spectra were recorded on a Shimadzu RF-5300PC spectrometer. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F₂₅₄ (Merck 5554).

The Data of 1-Zn

Synthesis: At room temperature, a solution of Zn(OAc)₂·2H₂O (39 mg) in MeOH (3 mL) was added to a solution of **1** (30 mg) in CH₂Cl₂ (30 mL). The progress of the reaction was monitored by TLC and MALDI-TOF-MS analyses. After 10 minutes, disappearance of **1** was confirmed and **1-Zn** was obtained quantitatively after aqueous work-up and purification on silica gel.

¹H NMR (CDCl₃) δ (ppm): 21.84 (br s, 2H, NH), 12.04 (br s, 2H, pyrrole- β), 8.70 (br s, 2H, pyrrole- β), 5.26 (br s, 4H, pyrrole- β), 4.92 (br s, 2H, pyrrole- β), 4.59 (br s, 2H, pyrrole- β), and 4.51 (br s, 2H, pyrrole- β).

¹⁹F NMR (CDCl₃) δ (ppm): -129.0 (s, 2F, *o*-F), -129.9 (d, *J* = 19 Hz, 2F, *o*-F), -135.7 (s, 2F, *o*-F), -137.0 (s, 2F, *o*-F), -138.0 (s, 2F, *o*-F), -139.8 (s, 2F, *o*-F), -141.0 (d, *J* = 17 Hz, 2F, *o*-F), -151.6 (br s, 2F, *p*-F), -153.2 (t, *J* = 19 Hz, 2F, *p*-F), -153.4 (t, *J* = 21 Hz, 2F, *p*-F), -154.0 (t, *J* = 21 Hz, 1F, *p*-F), -157.7 (m, 2F, *m*-F), -161.1 (m, 2F, *m*-F), -161.3 (m, 4F, *m*-F), -161.8 (m, 4F, *m*-F), and -162.0 (m, 2F, *m*-F).

ESI-MS (CH₃CN): m/z : 1767.0182 [M]⁺; m/z calcd. for C₇₇H₁₆F₃₅N₇Zn: 1767.0194.

UV-Vis (CH₂Cl₂): λ_{max} ($\epsilon \times 10^{-4}$) = 401 (5.6), 510 (2.2), and 642 nm (11.4).

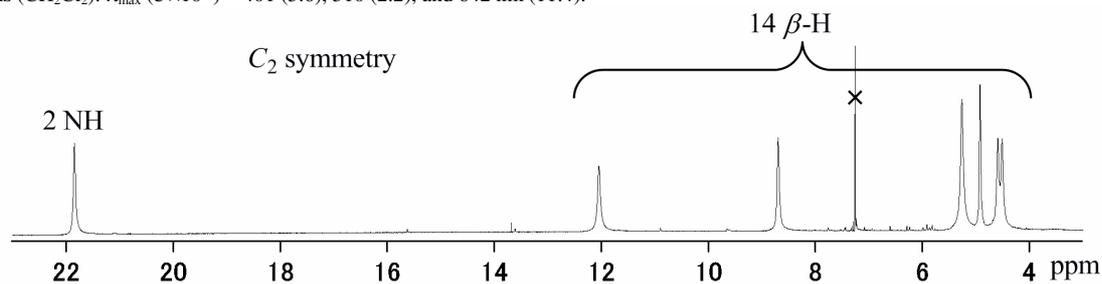


Figure S1. ¹H NMR spectrum of **1-Zn** in CDCl₃.

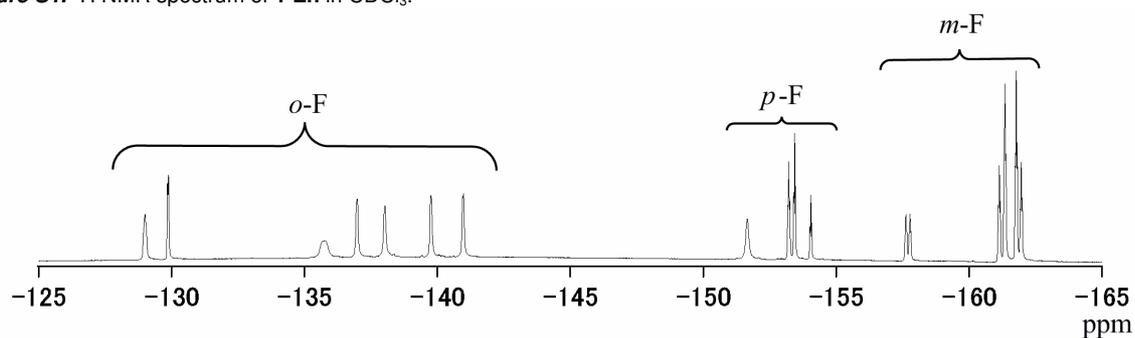


Figure S2. ¹⁹F NMR spectrum of **1-Zn** in CDCl₃.

The Data of **1-Cu**

Synthesis: At room temperature, a drop of MeOH solution of Cu(OAc)₂ (30 mg) was carefully added to a solution of **1** (30 mg) in CH₂Cl₂ (30 mL) until **1** was all consumed. The progress of the reaction was monitored by TLC and MALDI-TOF-MS analyses. Aqueous work-up and purification on silica gel yielded **1-Cu** quantitatively.

NMR spectra: too broad to analyze.

ESI-MS (CH₃CN): m/z : 1766.0218 [M]⁺; m/z calcd. for C₇₇H₁₆F₃₅N₇Cu: 1766.0199.

UV-Vis (CH₂Cl₂): λ_{max} ($\epsilon \times 10^{-4}$) = 396 (6.1) and 635 (8.4) nm.

SQUID measurement: The valence state of Cu(II) ion was elucidated (Figure S3).

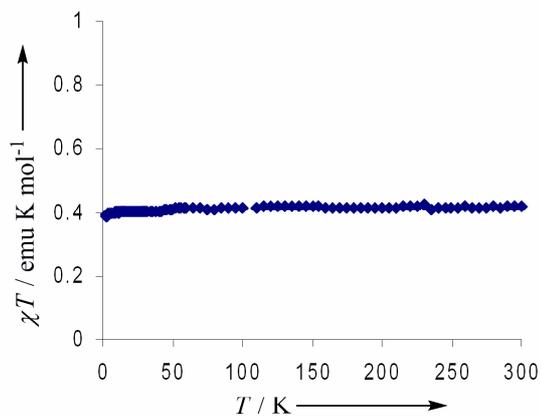


Figure S3. Temperature dependent magnetic susceptibility of **1-Cu**.

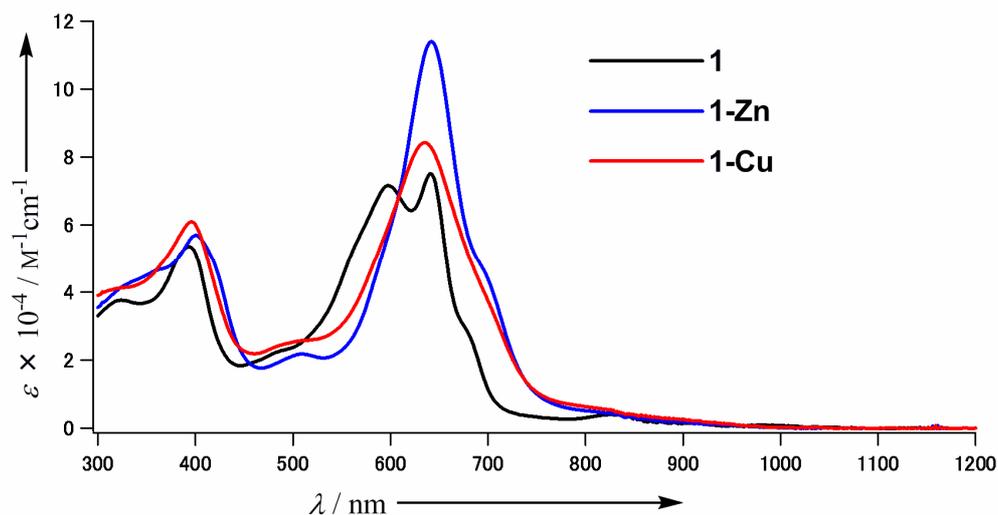


Figure S4. UV-vis Absorption spectra of **1**, **1-Zn**, and **1-Cu** in CH_2Cl_2 .

Attempted Extrusion Reaction of **1-Zn** and Purification of the Products

BBr_3 (0.70 mL, 100 equiv) was added to a dichloromethane solution of **1-Zn** (130 mg, 74 mmol) in the presence of ethyldiisopropylamine (1.92 mL, 150 equiv), and the reaction mixture was refluxed for 12 h under N_2 atmosphere. After the reaction was quenched by the addition of water, the products were extracted with ethyl acetate. The organic phase was neutralized by aqueous NaHCO_3 , and then dried over anhydrous Na_2SO_4 . After the removal of the solvent, the residue was subjected to silica gel column chromatography with a 15:1 mixture of hexane and ethyl acetate as eluent. The first eluted main blue fraction was evaporated to obtain a complicated mixture, which contains demetallated and/or decomposed heptaphyrins and a $\text{Zn}^{\text{II}}\text{-B}^{\text{III}}$ bis-metallated complex. The last brownish yellow fraction, which exhibited green fluorescence, was evaporated to give a trace of crude solid of hydroxyboron(III) complex of subporphyrin (<1%). The first blue fraction was further purified by silica gel column chromatography with a 3:1 mixture of hexane and dichloromethane to yield the $\text{Zn}^{\text{II}}\text{-B}^{\text{III}}$ bis-metallated complex (8 mg, 6%).

Data of $\text{Zn}^{\text{II}}\text{-B}^{\text{III}}$ Bis-metallated Complex

$^1\text{H NMR}$ (CDCl_3) δ (ppm): 7.50 (d, $J = 4.6$ Hz, 1H, pyrrole- β), 7.35 (d, $J = 4.6$ Hz, 1H, pyrrole- β), 7.20 (d, $J = 4.6$ Hz, 1H, pyrrole- β), 7.18 (d, $J = 5.8$ Hz, 1H, pyrrole- β), 7.08 (d, $J = 4.6$ Hz, 1H, pyrrole- β), 6.67 (d, $J = 4.6$ Hz, 1H, pyrrole- β), 6.46-6.45 (m, 2H, pyrrole- β), 6.36-6.34 (m, 2H, pyrrole- β), 6.14 (d, $J = 4.6$ Hz, 1H, pyrrole- β), 5.62 (m, 1H, pyrrole- β), 5.49 (m, 1H, pyrrole- β), 4.33 (d, $J = 4.6$ Hz, 1H, pyrrole- β), and -0.74 (s, 1H, OH).

$^{19}\text{F NMR}$ (CDCl_3) δ (ppm): -123.8 (dd, $J = 135, 23$ Hz, 1F, *o*-F), -137.2 (d, $J = 23$ Hz, 1F, *o*-F), -137.9 (d, $J = 23$ Hz, 1F, *o*-F), -138.2 (d, $J = 21$ Hz, 1F, *o*-F), -138.6 (m, 2F, *o*-F), -138.9 (m, 1F, *o*-F), -140.3 (m, 2F, *o*-F), -140.8 (d, $J = 25$ Hz, 1F, *o*-F), -141.2 (d, $J = 21$ Hz, 1F, *o*-F), -141.5 (d, $J = 21$ Hz, 1F, *o*-F), -143.6 (d, $J = 21$ Hz, 1F, *o*-F), -144.0 (d, $J = 23$ Hz, 1F, *o*-F), -152.9 (m, 2F, *p*-F), -153.1 (m, 2F, *p*-F), -153.4 (t, $J = 21$ Hz, 1F, *p*-F), -153.5 (t, $J = 21$ Hz, 1F, *p*-F), -153.6 (t, $J = 21$ Hz, 1F, *p*-F), -160.4 (m, 1F, *m*-F), -161.1 (m, 1F, *m*-F), -161.3 (m, 2F, *m*-F), -161.6 (m, 2F, *m*-F), -161.9 (m, 3F, *m*-F), -162.1 (m, 1F, *m*-F), -162.3 (m, 1F, *m*-F), -162.9 (m, 1F, *m*-F), -166.1 (m, 1F, *m*-F), and -166.9 (m, 1F, *m*-F).

$^{11}\text{B NMR}$ (CDCl_3) δ (ppm): -3.57 (br, s).

Extrusion Reaction of 1-Cu and Purification of The Products

BBr₃ (1.62 mL, 100 equiv) was added to a dichloromethane solution of **1-Cu** (300 mg, 170 mmol) in the presence of ethyldiisopropylamine (4.44 mL, 150 equiv), and the reaction mixture was stirred at room temperature for 24 h under N₂ atmosphere. After the reaction was quenched by the addition of water, the products were extracted with ethyl acetate. The organic phase was neutralized by aqueous NaHCO₃, and then dried over anhydrous Na₂SO₄. After the removal of the solvent, the residue was subjected to silica gel column chromatography with a 15:1 mixture of hexane and ethyl acetate as eluent. The first eluted red fraction was evaporated to obtain a Cu(II) complex of porphyrin **3-Cu** (23 mg, 13%). The last brownish yellow fraction, which exhibited blue-green fluorescence, was separated with a 10:1 mixture of hexane and ethyl acetate, and evaporated to give crude solid of hydroxyboron(III) complex of subporphyrin (~60%). Treatment of the product with refluxing methanol yielded crude solid of methoxyboron(III) complex of subporphyrin **2**. The crude product was further purified by repeated silica gel column chromatography with a 10:1 mixture of hexane and ethyl acetate to yield a pure sample of **2** (47 mg, 36%).

The Data of **2**

¹H NMR (CDCl₃) δ(ppm): 7.94 (s, 6H, pyrrole-β) and 0.84 (s, 3H, OMe).

¹⁹F NMR (CDCl₃) δ(ppm): -137.5 (dd, *J* = 24, 5.2 Hz, 3F, *o*-F), -139.4 (dd, *J* = 24, 5.2 Hz, 3F, *o*-F), -152.4 (t, *J* = 21 Hz, 3F, *p*-F), -161.7 (dt, *J* = 21, 8.6 Hz, 3F, *m*-F), and -161.8 (dt, *J* = 22, 8.6 Hz, 3F, *m*-F).

¹¹B NMR (CDCl₃) δ(ppm): -15.6 (br, s).

¹³C NMR (CDCl₃) δ(ppm): 146.4 (d, *J*_{C-F} = 130 Hz, *o*-C), 144.7 (d, *J*_{C-F} = 128 Hz, *o*-C), 142.3 (s, pyrrole-α), 142.0 (d, *J*_{C-F} = 142 Hz, *p*-C), 138.2 (d, *J*_{C-F} = 122 Hz, *m*-C), 137.8 (d, *J*_{C-F} = 127 Hz, *m*-C), 122.1 (s, pyrrole-β), 110.6 (t, *J*_{C-F} = 19 Hz, *ipso*-C), 103.9 (s, *meso*-C), and 46.7 (s, OMe).

ESI-MS: *m/z*: 794.0480 [*M*+Na]⁺; *m/z* calcd. for C₃₄H₉F₁₅N₃BONa 794.0497.

UV-Vis (CH₂Cl₂): λ_{max} (ε × 10⁻⁴) = 359 (12.3), 422 (sh.) (0.9), 449 (1.1), and 470 nm (0.6).

Fluorescence (CH₂Cl₂, λ_{ex} = 359 nm): λ_{max} = 487 and 517 nm.

Quantum yields (CH₂Cl₂): Φ_F = 0.12 (λ_{ex} = 359 nm, using *meso*-phenyl substituted subporphyrin as a reference); Φ_F = 0.094 (λ_{ex} = 420 nm, using Coumarin 6 as a reference).

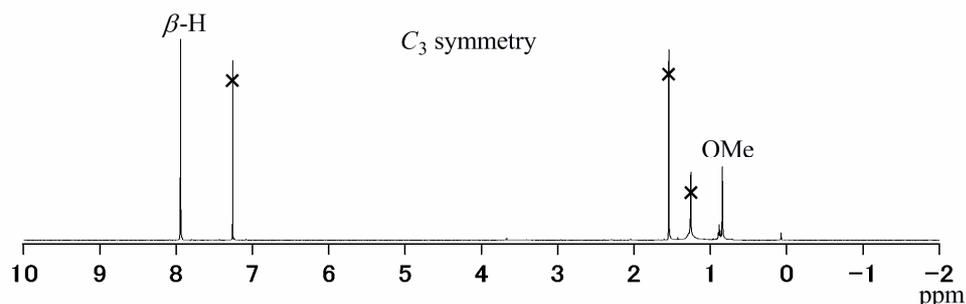


Figure S5. ¹H NMR spectrum of **2** in CDCl₃.

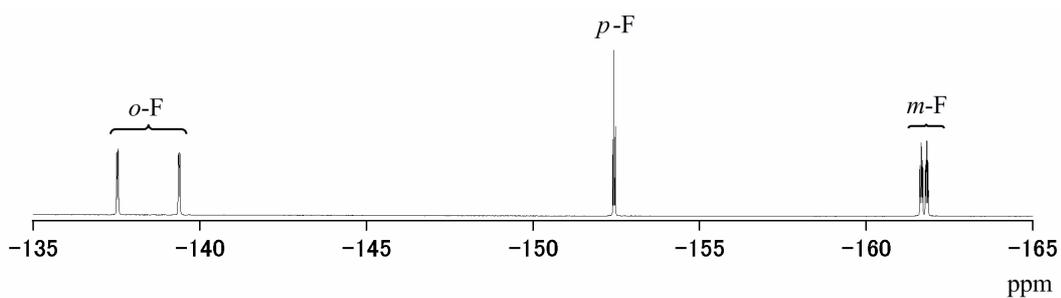


Figure S6. ^{19}F NMR spectrum of **2** in CDCl_3 .

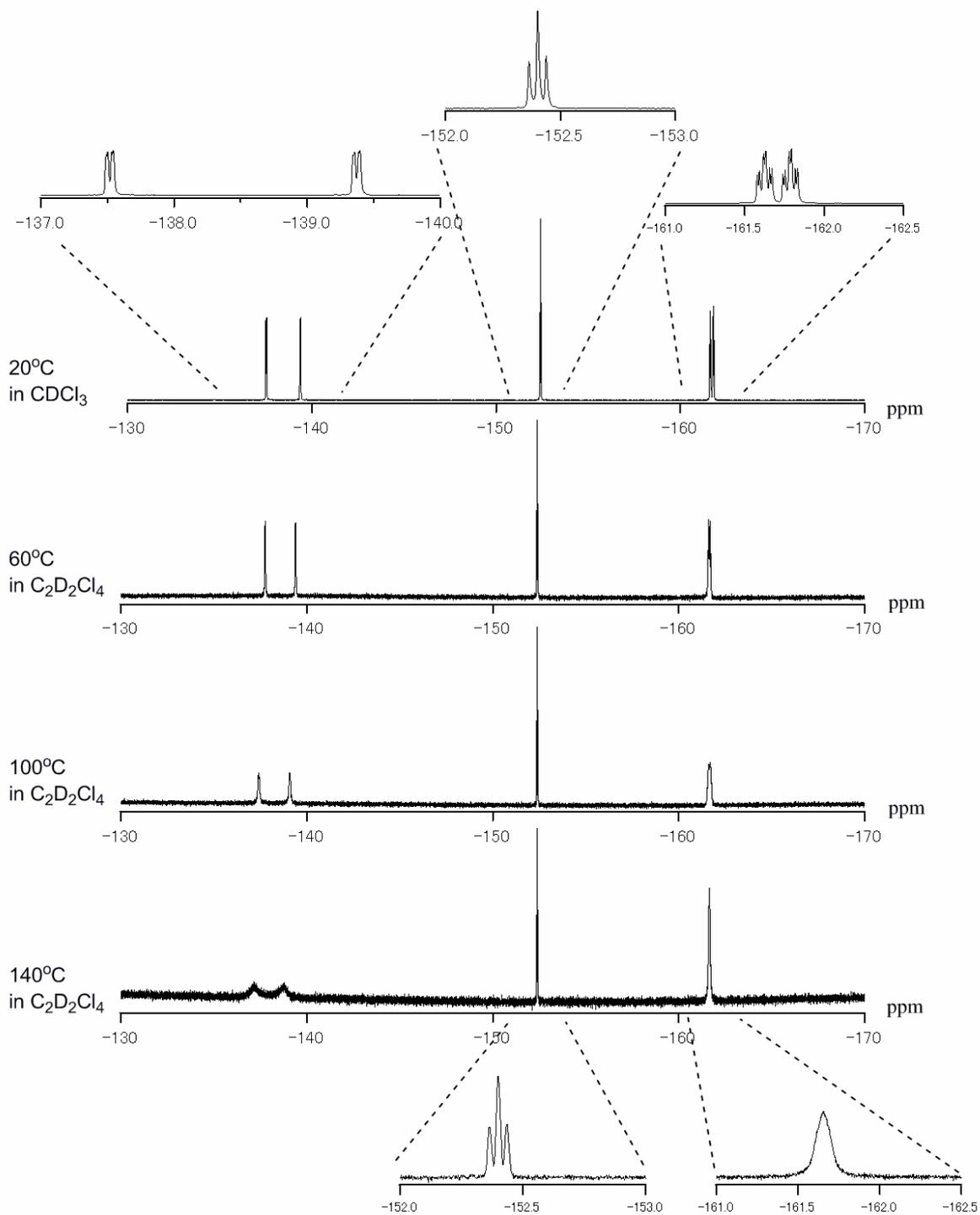


Figure S7. ^{19}F NMR spectra of **2** at various temperatures.

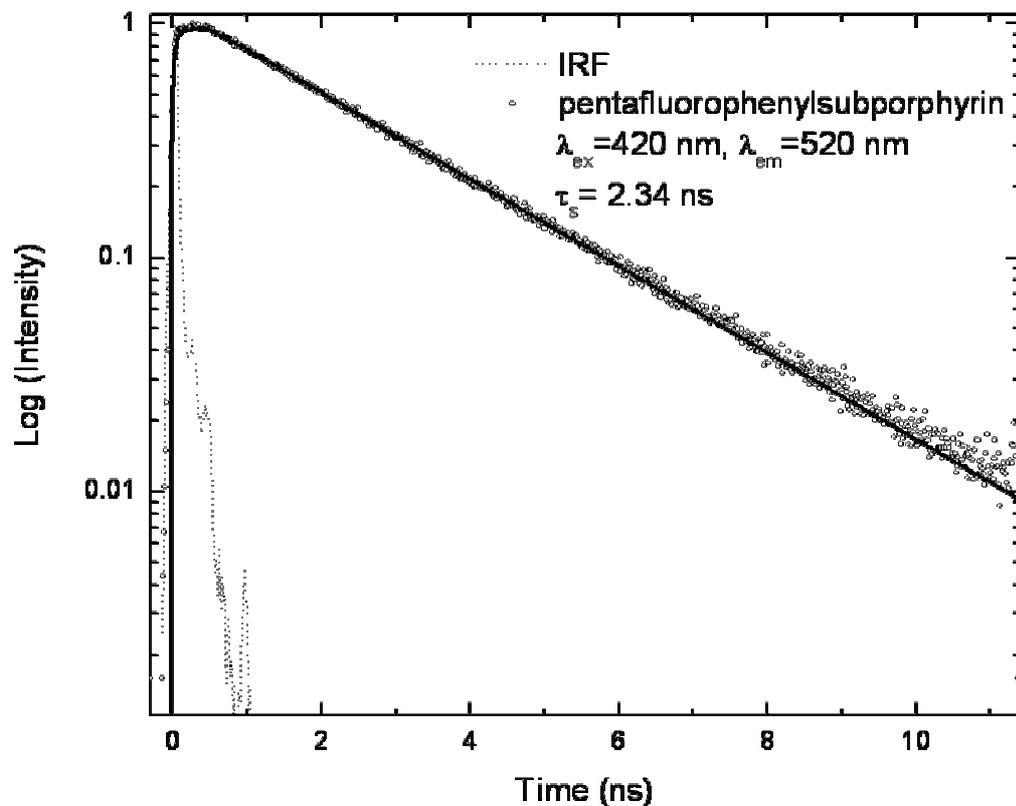


Figure S8. Fluorescence lifetime of **2** in CH_2Cl_2 monitored at 520 nm, following by the excitation at 420 nm femtosecond laser pulse. The data was measured by time-correlated single photon counting (TCSPC) method.

Possible Mechanism of The Extrusion Reaction

