Supporting Information

Synthesis and Properties of Boron Complexes of [14]triphyrins(2.1.1)

Daiki Kuzuhara,^{*a} ZhaoLi Xue,^a Shigeki Mori,^b Tetsuo Okujima,^c Hidemitsu Uno,^c Naoki Aratani^a and Hiroko Yamada^{*a,d}

^{*a*}Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma 630-0192, Japan,

^bDepartment of Molecular Science, Integrated Center for Sciences, Ehime University, Matsuyama 790-8577, Japan,

^cGraduate School of Science and Engineering, Ehime University, Matsuyama, 790-8577, Japan,

^dCREST, JST, Chiyoda-ku 102-0075, Japan,

Instrumentation and Materials

¹H NMR, ¹¹B NMR and ¹³C NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer at ambient temperature using tetramethylsilane as an internal standard. High-resolution ESI-TOF-MS was measured on a JEOL JMS-700 spectrometer. UV-vis spectra were measured on a JASCO UV/VIS/NIR Spectro-photometer V-570. Fluorescence spectra were measured on a JASCO FP-6600. Fluorescence quantum yields were measured on an Absolute PL Quantum Yield Measurement System C9920-02.

Materials Thin-layer chromatography (TLC) and gravity column chromatography were performed on Art. 5554 (Merck KGaA), and Silica Gel 60N (Kanto Chemical Co.), respectively. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification. For spectral measurements, spectral grade were purchased from Nacalai tesque Inc.

X–ray Analysis. X–ray crystallographic data were recorded on a Rigaku R-AXIS RAPID/S. The diffraction data were processed with Crystal Structure of the Rigaku program, solved with the SIR-97 program^{S1} and refined with the SHELX-97 program.^{S2}

Theoretical calculations All density functional theory calculations were achieved with the Gaussian09 program package. The geometry was fully optimized at the Becke's three-parameter hybrid functional combined with the Lee-Yang-Parr correlation functional abbreviated as the B3LYP level of density functional theory with 6-31G** basis set. Equilibrium geometries were verified by the frequency calculations, where no imaginary frequency was found. Based on the B3LYP/6-31G** optimized geometry, time dependent density functional theory (TDDFT) was conducted at the B3LYP/6-31G** level of theory.

Synthesis

Synthesis of 2-BF4



To a mixture of 1^{S3} (20 mg, 0.045 mmol) in toluene (2 ml) was added BPhCl₂ (0.4 ml) under an Ar atmosphere. After stirring for 5 h, the reaction was quenched with MeOH and the solvent was removed under a reduced pressure. The residue was purified by silica gel column chromatography (10% MeOH in CHCl₃) to give **2**•Cl. AgBF₄ (100 mg) then was added to **2**•Cl in CH₂Cl₂ (5 ml). The appeared precipitate was filtrated, and the filtrate was purified by recrystallization from MeOH/H₂O to give **2**•BF₄ as yellow solids. Yield: 91% (25 mg, 0.041 mmol). ¹H NMR (400 MHz, CDCl₃): δ 9.94 (s, 2H, *meso*), 9.87 (s, 2H, *meso*), 6.26 (m, 1H, ^{*p*}Ph), 5.99 (m, 2H, ^{*m*}Ph), 3.82-3.64 (m, 8H), 6.53 (s, 6H, -Me), 3.22 (m, 2H, ^{*m*}Ph), 2.01 (m, 4H), 1.71 (t, 6H, *J* = 7.3 Hz), 1.59 (m, 4H), 1.02 (t, 6H, *J* = 7.3 Hz) (ppm); ¹¹B NMR (128 MHz, CDCl₃): δ -14.2 (ppm); ¹³C NMR (125 MHz, CDCl₃): δ 150.5, 146.8, 145.2, 144.6, 144.1, 141.6, 126.8, 126.6, 120.1, 107.9, 34.5, 25.7, 22.9, 19.2, 17.7, 14.1, 11.5 (ppm); HRMS (ESI-TOF): calcd for C₃₆H₄₃BN₃ [M-BF₄]⁺ 527.3586, found 527.3589.

Synthesis of 4•BF₄



To a mixture of 3^{S4} (25 mg, 0.036 mmol) in toluene (10 ml) was added BPhCl₂ (0.3 ml) under an Ar atmosphere. After stirring for 5 h, the reaction was quenched with MeOH and the solvent was removed under a reduced pressure. The residue was purified by silica gel column chromatography (10% MeOH in CHCl₃) to give 4•Cl. AgBF₄ (100 mg) then was added to 2•Cl in CH₂Cl₂ (5 ml). The appeared precipitate was filtrated, and the filtrate was purified by recrystallization from CHCl₃/hexane to give 4•BF₄ as purple solids. Yield: 85% (26 mg, 0.030 mmol) ¹H NMR (400 MHz, CDCl₃): δ 8.14 (m, 2H, -Ph), 8.05-7.96 (m, 10H, -Ph), 7.77 (m, 2H, benzo), 7.68 (m, 2H, -Ph), 7.61 (m, 4H, -Ph), 7.55 (m, 2H, benzo), 7.52 (m, 2H, benzo), 7.44 (m, 2H, benzo), 7.12 (m, 2H, benzo), 6.88 (m, 2H, -Ph), 6.52 (m, 1H, ^{*p*}Ph), 6.40 (m, 2H, benzo), 6.28 (m, 2H, ^{*m*}Ph) 4.01 (m, 2H, ^{*o*}Ph) (ppm); ¹¹B NMR (128 MHz, CDCl₃): δ -11.7 (ppm); ¹³C NMR (128 MHz, CDCl₃): δ 144.4, 143.5, 143.2, 140.0, 139.0, 135.9, 135.4, 134.5, 133.9, 131.5, 131.5, 130.9, 130.8, 130.7, 130.6, 130.5, 129.7, 129.0, 127.7, 127.5, 127.3, 126.9, 125.9, 125.6, 122.2 (ppm); HRMS (ESI-TOF): calcd for C₅₈H₃₇BN₃ [M-BF₄]⁺ 785.3117, found 785.3117.



Figure S1 Kohn-Sham orbitals and calculated energy levels of 1a, $2a^+$, 3 and 4^+ at the B3LYP/6-31G** level using Gaussian 09 program.



Figure S2. Absorption spectra in CH_2Cl_2 and calculated TD-DFT oscillator strengths of **2-BF**₄.



Figure S3. Absorption spectrum in CH₂Cl₂ and calculated TD-DFT oscillator strengths of **4-BF**₄.



Figure S4. Cyclic voltammogram of $2 \cdot BF_4$ (top) and $4 \cdot BF_4$ (bottom) in acetonitrile containing the 0.1 M (nBu)₄NPF₆ as supporting electrolyte. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgNO₃.



Figure S5 H-H COSY spectrum of **2-BF**₄ in CDCl₃.



Figure S6. ¹³C NMR spectrum of **2-BF**₄ in CDCl₃.



Figure S7 H-H COSY spectrum of **4**•**BF**₄ in CDCl₃.



Figure S8. ¹³C NMR spectrum of **4**•**BF**₄ in CDCl₃.



Figure S8. Crystal structure of 2-BF₄. Thermal ellipsoids represent 30% probability.



Figure S9. Crystal structure of **4-BF**₄. Thermal ellipsoids represent 30% probability.

References

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