Supplementary Material (ESI) for Chemical Communications

Supporting Information

Multiple conformational changes of *β*-tetraphenyl *meso*-hexakis(pentafluorophenyl) substituted [26] and [28]hexaphyrins(1.1.1.1.1.1)

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1. General Experimental Methods

All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 was obtained by refluxing and distillation over CaH_2. Silica gel column chromatography was performed on Wakogel C-200, C-300 and C-400, and flash column chromatography was performed on Merck Kieselgel 60 H. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (Merck 5554). UV-visible spectra were recorded on a Shimadzu UV-3100PC spectrometer. ^{1}H NMR (600 MHz) and ^{19}F NMR (565 MHz) spectra were taken on a JEOL ECA-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ as internal reference for ^{1}H (δ = 7.260 ppm) and to CH_2Cl_2 as internal reference for ^{1}H (δ = 5.320 ppm), and hexafluorobenzene as external reference for ^{19}F (δ = -162.9 ppm). Mass spectra were recorded on a Shimadzu KRATOS KOMPACT MALDI4 using positive-MALDI-TOF method and on a BRUKER microTOF using positive or negative mode ESI-TOF method of acetonitrile solutions. X-ray single crystal diffraction analyses were performed on a Rigaku-Raxis imaging plate system or a BRUKER-APEX X-Ray diffractometer equipped with a large area CCD detector.

2. Synthetic Procedures

β-Tetraphenyl *meso*-hexakis(pentafluorophenyl)[26]hexaphyrin(1.1.1.1.1.1) **3**

To a solution of diacyldipyrromethane (562.2 mg, 0.80 mmol) in THF (40 mL)/MeOH (10 mL) was added slowly $NaBH_4$ (3.03 g, 80.0 mmol) and the resulting solution was stirred for 2 h. The reaction was quenched by addition of water and the product was extracted with CH_2Cl_2. The organic phase was washed with water and brine and dried over Na_2SO_4. The solvent was removed by a rotary evaporator to leave residue, to which 3,4-diphenylpyrrole prepared by deprotection of 3,4-diphenyl-N-TIPS-pyrrole (299.8 mg, 0.80 mmol) with $(n\text{-Bu})_4NF{\bullet}3H_2O$ (214.3 mg, 0.82 mmol) in THF (2.4 mL) and CH_2Cl_2 (30 mL) were added and then the condensation was started by addition of 2.5 M methanesulfonic acid (MSA, 1.0 mL). After this solution was stirred for 1 h, DDQ (550 mg, 2.42 mmol) was added and the resulting solution was stirred for additional 3 h and neutralized by the addition of triethylamine. The reaction mixture was passed through a short aluminum column with CH_2Cl_2 and purified by silica gel column with 30% CH_2Cl_2/hexane ~ CH_2Cl_2. The main blue fraction was collected and recrystallized from a mixture of CH_2Cl_2 and hexane to give **3** as green solids (138 mg, 20%).

3A (rectangular shape): ^{1}H NMR (600 MHz, CD_2Cl_2, –60 °C) δ [ppm] = 9.02 (d, J = 5.2 Hz, 2H, *β*-H), 8.67 (d, J = 4.6 Hz, 2H, *β*-H), –0.45 (d, J = 3.4 Hz, 2H, *β*-H), –0.53 (s, 2H, N-H), and –0.56 (d, J = 3.4 Hz, 2H, *β*-H).

3B (figure-eight shape): ^{1}H NMR (600 MHz, CD_2Cl_2, –60 °C) δ [ppm] = 9.01 (s, 2H, N-H), 6.84 (d, J = 3.5 Hz, 2H, *β*-H), 6.72 (d, J = 2.3 Hz, 2H, *β*-H), 5.44 (d, J = 4.6 Hz, 2H, *β*-H), and 4.31 (d, J = 4.6 Hz, 2H, *β*-H).

unassighned signals (*β*-phenyl groups): ^{1}H NMR (600 MHz, CD_2Cl_2, –60 °C) δ [ppm] = 7.76 (br, s, 2H, phenyl-H), 7.60 (br, 4H, phenyl-H), 7.42 (br, 4H, phnyl-H), 7.36 (m, 6H, phenyl-H), 7.25 (m, 8H, phenyl-H), 7.07-7.14 (m, 10H, phenyl-H), 7.01 (t, J = 7.4 Hz, 2H, phenyl-H), 6.86 (br, 2H, phenyl-H) 6.51 (br, 2H, Phenyl-H).

^{19}F NMR (565 MHz, CD_2Cl_2, –60 °C) δ [ppm] = –136.59 (d, J = 20.7 Hz, 4F, *o*-F), –136.99 (br, 6F, *o*-F), –137.84 (br, 2F, *o*-F), –136.59 (d, J = 20.7 Hz, 2F, *o*-F), –136.99 (br, 6F, *o*-F), –137.84 (br, 2F, *o*-F), –138.54 (d, J = 20.7 Hz, 2F, *o*-F), –138.64 (d, J = 20.7 Hz, 2F, *o*-F), –138.83 (d, J = 20.7 Hz, 2F, *o*-F), –139.31 (br, 2F, *o*-F), –139.62 (d, J = 24.2 Hz, 2F, *o*-F), –151.96 (t, J = 20.7 Hz, 2F, *p*-F), –152.10 (t, J = 20.7 Hz, 2F, *p*-F), –152.26 (t, J = 20.7 Hz, 2F, *p*-F), –152.51 (br, 2F, *p*-F), –155.29 (t, J = 20.7 Hz, 2F, *p*-F), –162.53–-162.13 (m, 12F, *m*-F (R)), –163.09 (m, 2F, *m*-F (F)), –163.32 (br, 4F, *m*-F (F)), –164.94 (m, 4F, *m*-F (F)), and –166.23 (br, 2F, *m*-F (F)).

UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]) = 355(42400), 580(110000), 619(121000), 731(10900), 796(11300), 896(7750), 946(sh, 4790); ESI-TOF-MS (positive-mode) (%intensity): $C_{90}H_{31}F_{30}N_6$ ([M + H]$^+$): calcd: 1765.2126, found: 1765.2177 (100%). Chemical shifts of NMR signals thought to be due to the rectangular conformation (R) were indicated in

red and those thought to be due to the figure-eight conformation (F) were indicated in blue. It was hard to determine which signals were due to which protons of *β*-phenyl groups, because the chemical sifts and intensity of the signals were similar.

β-Tetraphenyl *meso*-hexakis(pentafluorophenyl)[28]hexaphyrin(1.1.1.1.1.1) **4**

To a solution of **3** in CH_2Cl_2 was added 10 equiv of $NaBH_4$. After the reaction was quenched by addition of water, the product was extracted with CH_2Cl_2. The organic extract was passed through a short alumina column. Recrystallization from hexane afforded **4** quantitatively.

4A: ^{1}H NMR (600 MHz, $CDCl_3$, room temperature) δ [ppm] = 14.68 (s 2H, NH), 14.05 (s, 2H, NH), 8.42 (d, J = 6.9 Hz, 2H, phenyl-H), 7.47 (t, J = 7.2 Hz, 2H, phenyl-H), 7.32 (t, J = 7.3 Hz, 2H, phenyl-H), 6.53-7.13 (m, 14H phenyl-H), 6.41 (d, J = 5.5 Hz, 2H, *β*-H), 6.24 (d, J = 4.8 Hz, 2H, *β*-H), 5.79 (d, J = 5.5 Hz, 2H, *β*-H), and 5.56 (d, J = 4.8 Hz, 2H, *β*-H); ^{19}F NMR (565 MHz, $CDCl_3$, room temperature) δ [ppm] = –135.70 (d, J = 20.7 Hz, 2F, *o*-F), –137.57 (dd, J^1 = 24.2 Hz, J^2 = 6.9 Hz, 2F, *o*-F), –138.42 (s, 2F, *o*-F), –138.66 (dd, J^1 = 24.2 Hz, J^2 = 6.9 Hz, 2F, *o*-F), –139.07 (m, 2F, *o*-F), –139.73 (d, J = 24.2 Hz, 2F, *o*-F), –152.33 (t, J = 19.0 Hz, 2F, *p*-F), –153.03 (t, J = 20.7 Hz, 2F, *p*-F), –154.16 (t, J = 20.7 Hz, 2F, *p*-F), –159.82 (t, J = 24.2 Hz, 2F, *m*-F), –161.5-–161.2 (m, 4F, *m*-F), –162.16 (dd, J^1 = 24.2 Hz, J^2 = 6.9, 2F, *m*-F), and –162.60 (t, 2F, J = 20.7 Hz, *m*-F).

4B: ^{1}H NMR (600 MHz, $CDCl_3$, room temperature) δ [ppm] = 16.12 (br, 2H, NH), 13.15 (br, 2H, NH), 8.20 (br, 2H, phenyl-H), 6.53-7.13 (m, 16H, phenyl-H + 6H, *β*-H), and 6.21 (br, 2H, *β*-H); ^{19}F NMR (565 MHz, $CDCl_3$, room temperature) δ [ppm] = –136.83(br, 2F, *o*-F), –137.02 (br, 2F, *o*-F), –137.38 (br, 2F, *o*-F), –138.60 (br, 2F, *o*-F), –139.45 (br, 2F, *o*-F), –140.01 (br, 2F, *o*-F), –152.33 (br, 4F, *p*-F), –155.47 (br, 2F, *p*-F), –159.53 (br, 2F, *m*-F), –161.5-–161.2 (m, 2F, *m*-F), –161.93 (br, 2F, *m*-F), –162.98 (br, 2F, *m*-F), and –163.17 (br, 2F, *m*-F).

UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]) = 321(40300), 529(77100), 595(61400); ESI-TOF-MS (positive-mode) (%intensity): $C_{90}H_{33}F_{30}N_6$ ([M + H]$^+$): calcd: 1767.2282, found: 1767.2742 (100%).

Ratio of the intensity of two conformational isomers was revealed as 1: 0.72 for the major conformation (**4A**) and the minor one (**4B**).

β-Tetraphenyl *meso*-hexakis(pentafluorophenyl)[28]hexaphyrin(1.1.1.1.1.1)-TFA complex **4-TFA$_1$** and **4-TFA$_2$**.

TFA titration in NMR measurement was conducted by using highly diluted TFA or pure TFA depending upon the case. Diluted TFA solution in CD_2Cl_2 was prepared by dilution of distilled TFA (135 μL, 1.77 mmol) in 2.0 mL of CD_2Cl_2. The hexaphyrin **4** (7.8 mg, 4.4 μmol) was added to CD_2Cl_2 (0.60 mL) in a NMR sample tube, and titrated by 5.0 μL solution (4.4 μmol, 1.0 equivalent TFA for **4**) until the total TFA amounts to 5 equivalent, and next, titrated by 25 μl (22 μmol, 5.0

equivalent TFA for **4**) until the total TFA amounts to 30 equivalent. Finally, the titration was conducted by 5μL pure TFA (6.6 mmol, 15 equivalent TFA for **4**) until the total TFA amounts to 90 equivalent.

TFA titration in UV/vis absorption spectra was conducted by using highly diluted TFA (solution A**;** 10 mM) or diluted TFA (solution B; 100 mM) depending upon the case. Solution A and B was prepared by dilution of distilled TFA in CH_2Cl_2. A solution of **3** in 3 mL of CH_2Cl_2 was titrated by solution A until [TFA] = 6.8×10^{-4} M (total 150 equivalent). Next, it was titrated by solution B until [TFA] = 8.2×10^{-3} M (total 2000 equivalent). Further addition of pure TFA was carried out, but the absorption spectra did not change. The concentration of TFA is important in the UV/vis absorption measurement around [**3**] = 10^{-6} M concentration, while TFA equivalent is important in the ^{1}H-NMR measurement around [**3**] = 10^{-3} M concentration.

4-TFA$_1$: ^{1}H NMR (600 MHz, CD_2Cl_2, –80 °C) δ [ppm] = 14.02 (s, 1H, outer N-H), 13.92 (s, 1H, outer N-H), 8.76 (d, J = 7.6 Hz, 1H, outer β-H), 8.34 (d, J = 8.2 Hz, 1H, outer β-H), 6.6-8.3 (m, phenyl-H + outer β-H), 6.54 (d, J = 7.7 Hz, 1H, outer β-H), 6.38 (d, J = 7.1 Hz, 1H, outer β-H), 5.82 (d, J = 8.3, 1H, outer β-H), 5.75(d, J = 6.4, 1H, outer β-H), 5.57 (s, 1H, inner N-H), 5.54 (d, J = 7.3, 1H, β-H), 5.37 (s, 1H, N-H), 4.88 (s, 1H, N-H), 4.49 (s, 1H, N-H), 0.69 (s, 1H + 1H, inner β-H), –0.15 (s, 1H, inner N-H), –0.99 (s, 1H, inner N-H), –1.58 (s, 1H, inner N-H), –2.23 (s, 1H, inner N-H), –3.03 (s, 1H, inner β-H), and –3.07 (s, 1H, inner β-H). UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]) = 390 (44700), 491 (33700), 617 (246000), 828 (12200), 869 (15200), 928 (10100), and 988 (6320).

4-TFA$_2$: ^{1}H NMR (600 MHz, CD_2Cl_2, –80 °C) δ [ppm] = 13.65 (s, 1H, outer N-H), 13.52 (s, 1H, outer N-H), 8.73 (d, J = 7.6 Hz, 1H, outer β-H), 8.34 (d, J = 8.2 Hz, 1H, outer β-H), 6.6-8.3 (m, phenyl-H + outer β-H), 6.53 (d, J = 7.3 Hz, 1H, β-H), 6.37 (d, J = 7.3 Hz, 1H, β-H), 5.83 (d, J = 7.3, 1H, β-H), 5.67(d, J = 7.3 , 1H, β-H), 5.35 (s, 1H, inner N-H), 5.47 (d, J =7.2 , 1H, β-H), 5.20 (s, 1H, inner N-H), 4.86 (s, 1H, inner N-H), 4.49 (s, 1H, inner N-H) 1.71 (s, 1H, inner N-H), 0.72 (s, inner β-H), 0.66 (s, inner β-H), 0.57 (s, 1H, inner N-H), –0.13 (s, 1H, inner N-H), –0.98 (s, 1H, inner N-H), –1.78 (s, 1H, inner N-H), –2.15 (s, 1H, inner N-H), –3.00 (s, 1H, inner β-H), and –3.08 (s, 1H, inner β-H). UV/Vis (CH_2Cl_2): λ_{max}[nm] (ε [M^{-1} cm^{-1}]) = 391 (45600), 631 (256000), 861 (18700), and 967 (9420). For **4-TFA$_1$** and **4-TFA$_2$**, the spectral assignments were difficult because of the similarity of the chemical shifts and intensities of signals.

3. ^{1}H- and ^{19}F-NMR Spectra

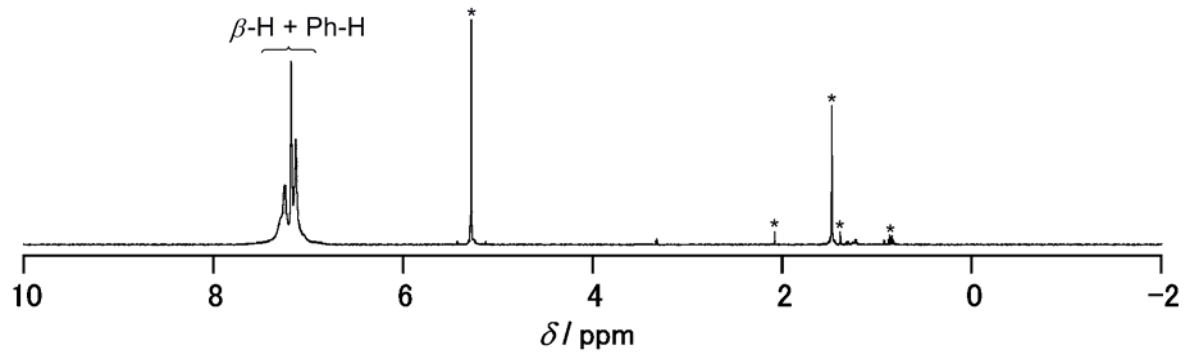

Figure S1. ^{1}H-NMR spectrum of **3** in CD_2Cl_2 at room temperature.

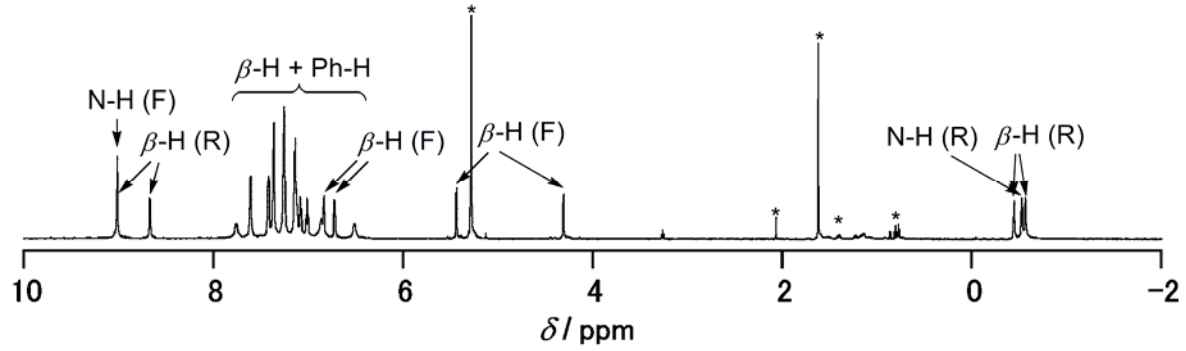

Figure S2. ^{1}H-NMR spectrum of **3** in CD_2Cl_2 at –60 °C. The signals due to the rectangular conformation and figure-eight conformation are designated as (R) and (F), respectively.

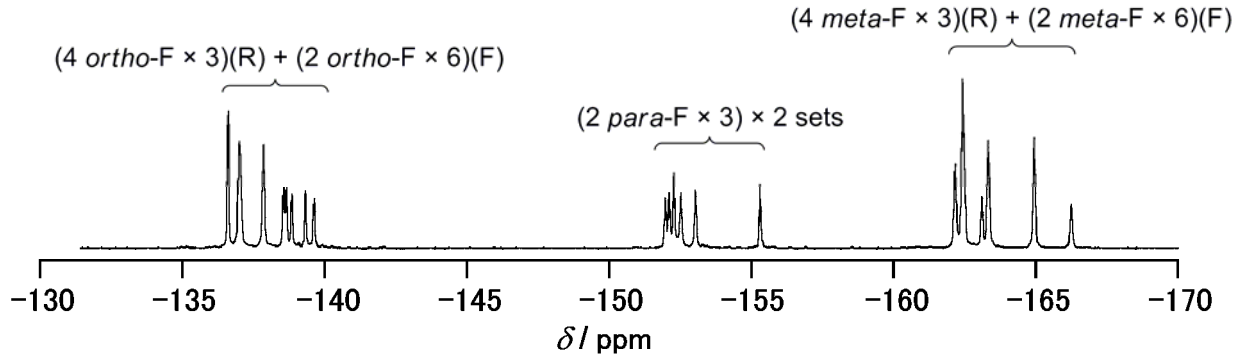

Figure S3. ^{19}F-NMR spectrum of **3** in CD_2Cl_2 at –60 °C. The signals due to the rectangular conformation and figure-eight conformation are designated as (R) and (F), respectively.

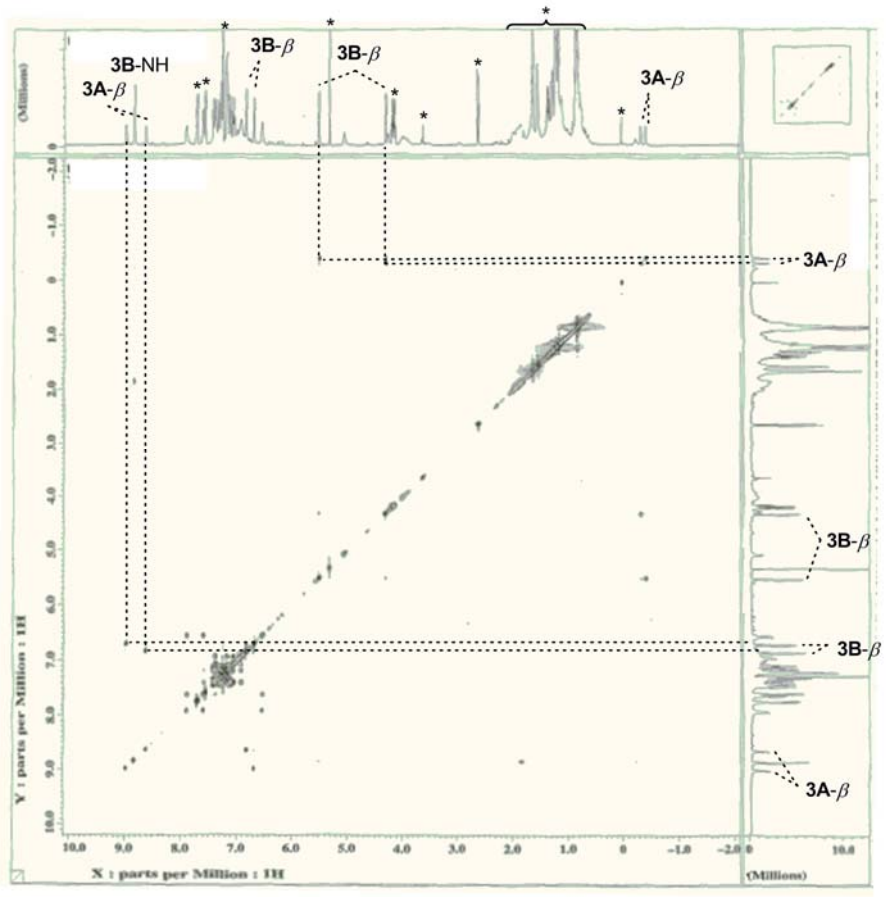

Figure S4. ^{1}H-^{1}H NOESY NMR spectrum of **3** in $CDCl_3$ at –60 °C. Correlation between the signals due to *β*-protons of **3A** and those of **3B** were observed, indicating that the conformational exchange between **3A** and **3B** is slow enough to see two separate sets of resonances but still exist at –60 °C.

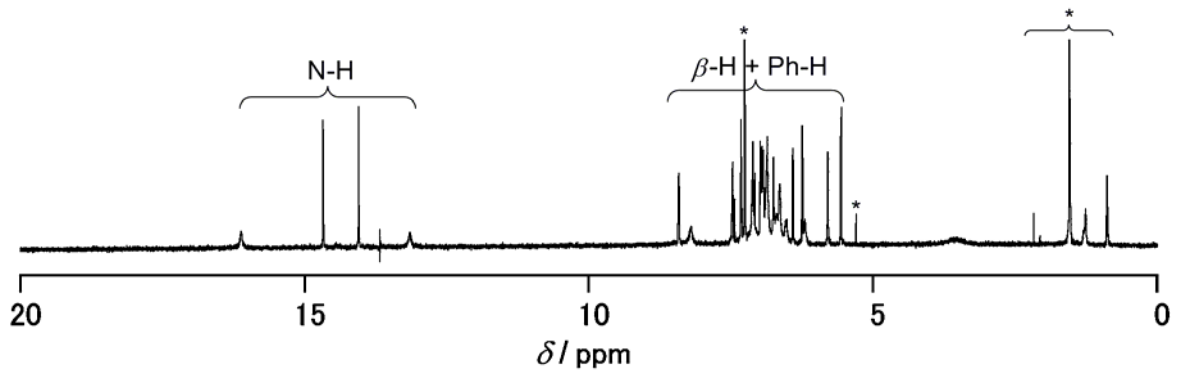

Figure S5. ^{1}H-NMR spectrum of **4** in $CDCl_3$ at room temperature. Two sets of signals (sharp ones and broad ones) were observed.

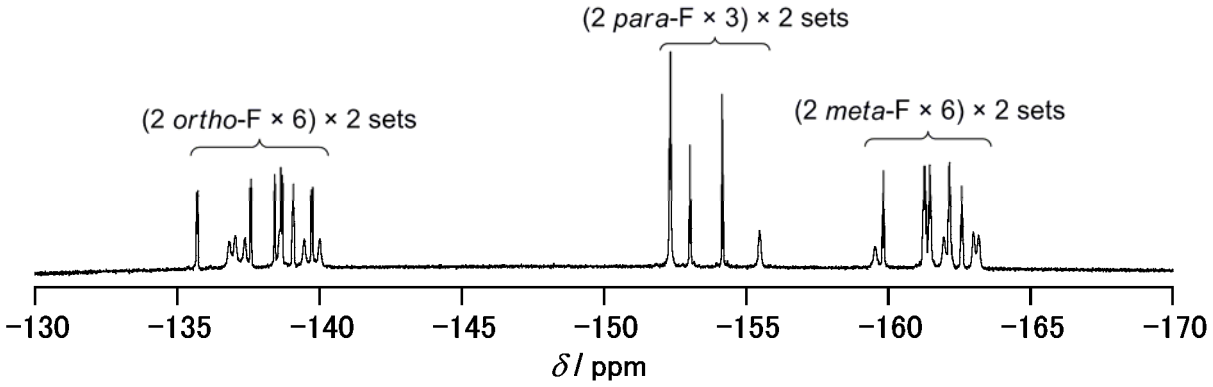

Figure S6. ^{19}F-NMR spectrum of **4** in $CDCl_3$ at room temperature.

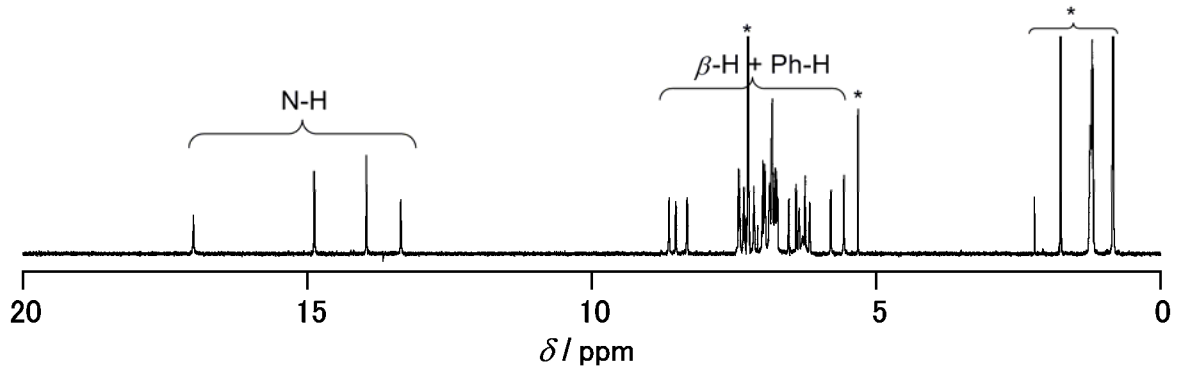

Figure S7. ^{1}H-NMR spectrum of **4** in $CDCl_3$ at –60 °C.

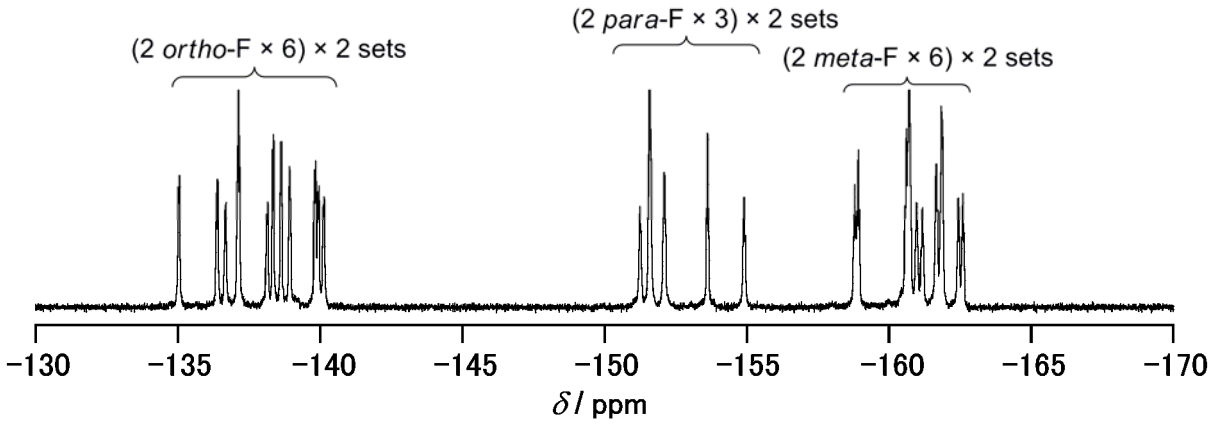

Figure S8. ^{19}F-NMR spectrum of **4** in $CDCl_3$ at –60 °C.

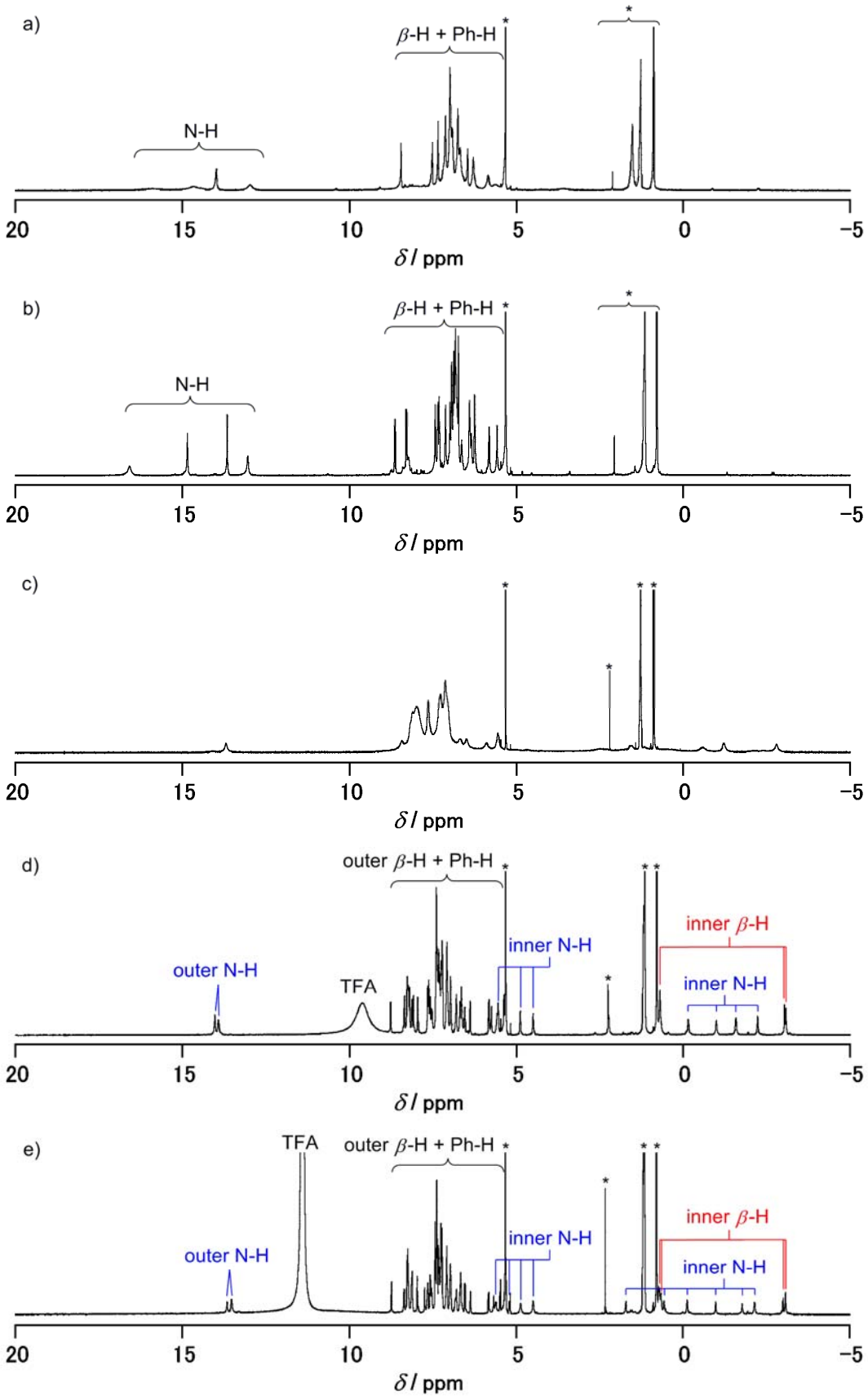

Figure S9. ^{1}H-NMR spectra for the TFA titration experiments of **2** in CD_2Cl_2; a) without TFA at room temperature, a) without TFA at –80 °C, c) with ten equivalent of TFA at room temperature, d) with ten equivalent of TFA at –80 °C, e) with thirty equivalent of TFA at –80 °C.