

Supporting Information
for
A β -to- β 2,5-Thienylene-bridged Cyclic Porphyrin Tetramer: Its Rational Synthesis and
1:2 Binding Mode with C₆₀

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Instrumentation and Materials

^1H NMR (600 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 ^1H NMR ($\delta = 7.260$ ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Mass spectra were recorded on a Shimadzu AXIMA-CFRplus using positive-MALDI-TOF method with matrix. X-Ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-300). Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (Merck 5554). Recycling preparative GPC-HPLC was carried out on a JAI LC-908 using preparative JAI-GEL-2.5H, 3H, and 4H columns (chloroform eluant; flow rate 3.8 mL min^{-1}). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedure

Synthesis of 2Br: A toluene-DMF solution (4 mL/2 mL) of **1** (140 mg, 0.124 mmol), 2,5-dibromothiophene (2.0 μL , 0.0177 mmol), $\text{Pd}_2(\text{dba})_3$ (1.6 mg, 0.00177 mmol), PPh_3 (1.9 mg, 0.007 mmol), Cs_2CO_3 (11.5 mg, 0.035 mmol), and CsF (5.4 mg, 0.035 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 24 h. The reaction mixture was diluted with CH_2Cl_2 , washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC and recrystallization with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ provided **2B** (containing 10% mono-borylated dimer) in ca. 80% yield as a dark red solid. A toluene-DMF solution (2 mL/1 mL) of **2B** (20.8 mg), 2,5-dibromothiophene (0.050 mL, 0.44 mmol), $\text{Pd}_2(\text{dba})_3$ (0.34 mg, 0.00038 mmol), PPh_3 (0.4 mg, 0.0015 mmol), Cs_2CO_3 (6.5 mg, 0.020 mmol), and CsF (3.0 mg, 0.020 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 24 h. The reaction mixture was diluted with CH_2Cl_2 , washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC and silica-gel column chromatography (CH_2Cl_2 -hexane as an eluent)

and recrystallization with CH₂Cl₂/MeOH furnished **2Br** (13 mg, 0.006 mmol) in 48% yield (in 2 steps) as a dark red solid. **2B**: ¹H NMR (CDCl₃): δ 11.70 (s, 2H, *meso*-H), 9.58 (s, 2H, β-H), 9.26 (s, 2H, β-H), 8.99 (d, *J* = 4.6 Hz, 2H, β-H), 8.94 (d, *J* = 4.6 Hz, 2H, β-H), 8.84 (m, 4H, β-H), 8.61 (s, 2H, thiophene-H), 8.20 (d, *J* = 1.8 Hz, 4H, Ar-*o*-H), 8.09 (d, *J* = 1.8 Hz, 4H, Ar-*o*-H), 8.08 (d, *J* = 1.8 Hz, 4H, Ar-*o*-H), 7.80 (m, 6H, Ar-*p*-H), 1.58 (s, 36H, *tert*-butyl), 1.56 (s, 36H, *tert*-butyl), 1.55 (s, 36H, *tert*-butyl), 1.43 (s, 24H, *Bpin*), and -2.47 (s, 4H, NH) ppm; MS (MALDI-TOF-MS): *m/z* = 2082.40, calcd for C₁₄₀H₁₇₀B₂N₈O₄S = 2082.33 [M]⁺. **2Br**: ¹H NMR (CDCl₃): δ 11.20 (s, 2H, *meso*-H), 9.38 (s, 2H, β-H), 9.08 (s, 2H, β-H), 9.03 (d, *J* = 4.6 Hz, 2H, β-H), 9.01 (d, *J* = 5.0 Hz, 2H, β-H), 8.98 (m, 4H, β-H), 8.47 (s, 2H, thiophene-H), 8.29 (d, *J* = 1.8 Hz, 4H, Ar-*o*-H), 8.21 (d, *J* = 1.8 Hz, 4H, Ar-*o*-H), 8.16 (d, *J* = 1.8 Hz, 4H, Ar-*o*-H), 7.92 (t, *J* = 1.8 Hz, 2H, Ar-*p*-H), 7.89 (t, *J* = 1.8 Hz, 2H, Ar-*p*-H), 7.88 (d, *J* = 3.6 Hz, 2H, thiophene-H), 7.87 (t, *J* = 1.8 Hz, 2H, Ar-*p*-H), 7.08 (d, *J* = 3.6 Hz, 2H, thiophene-H), 1.65 (s, 36H, *tert*-butyl), 1.63 (s, 36H, *tert*-butyl), 1.60 (s, 36H, *tert*-butyl), and -2.38 (s, 4H, NH) ppm; MS (MALDI-TOF-MS): *m/z* = 2152.90, calcd for C₁₃₆H₁₅₀Br₂N₈S₃ = 2152.95 [M]⁺.

Synthesis of 4H: A toluene-DMF solution (2 mL/1 mL) of **2Br** (13 mg, 0.006 mmol), **2B** (12.5 mg, 0.006 mmol), Pd₂(dba)₃ (0.92 mg, 0.001 mmol), PPh₃ (1.1 mg, 0.004 mmol), Cs₂CO₃ (3.9 mg, 0.012 mmol), and CsF (1.8 mg, 0.012 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 48 h. The reaction mixture was diluted with CH₂Cl₂, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC and silica-gel column chromatography (CH₂Cl₂-hexane as an eluent) and recrystallization with CH₂Cl₂/MeOH afforded **4H** (12 mg, 0.0031 mmol) in 52% yield as a dark red solid. **4H**: ¹H NMR (CDCl₃, rt): δ 11.27 (s, 4H, *meso*-H), 9.07 (s, 8H, β-H), 8.81 (d, *J* = 5.0 Hz, 8H, β-H), 8.77 (d, *J* = 5.0 Hz, 8H, β-H), 8.67 (s, 8H, thiophene-H), 8.06 (t, *J* = 1.8 Hz, 8H, Ar-*o*-H), 8.04 (t, *J* = 1.8 Hz, 4H, Ar-*o*-H), 7.97 (t, *J* = 1.8 Hz, 8H, Ar-*o*-H), 7.89 (t, *J* = 1.8 Hz, 4H, Ar-*o*-H), 7.73 (t, *J* = 1.8 Hz, 4H, Ar-*p*-H), 7.71 (t, *J* = 1.8 Hz, 8H, Ar-*p*-H), 1.52 (s, 72H, *tert*-butyl), 1.49 (s, 36H, *tert*-butyl), 1.41 (s, 36H, *tert*-butyl), 1.38 (s, 72H, *tert*-butyl), and -2.60 (s, 8H, NH) ppm; UV/Vis (CH₂Cl₂): λ_{max} (ε [M⁻¹ cm⁻¹]) =

428 (270000), 531 (78000), 603 (32000), and 657 (6000) nm; MS (MALDI-TOF-MS): $m/z = 3821.30$, calcd for $C_{264}H_{296}N_{16}S_4 = 3821.26 [M]^+$; Fluorescence (CH_2Cl_2 , $\lambda_{ex} = 428$ nm): $\lambda_{max} = 666$ nm. $\Phi_F = 0.032$.

Synthesis of 4Ni: **4H** (5.0 mg) was added to a round-bottomed 50-mL flask with a magnetic bar, and dissolved in toluene. Excess nickel(II) acetylacetonate was added. After stirring for 5 h, the reaction mixture was passed through an alumina column, evaporated and recrystallized from methanol and dichloromethane. **4Ni** was obtained quantitatively. **4Ni:** 1H NMR ($CDCl_3$, rt): δ 10.81 (s, 4H, *meso*-H), 8.93 (s, 8H, β -H), 8.70 (d, $J = 5.0$ Hz, 8H, β -H), 8.69 (d, $J = 5.0$ Hz, 8H, β -H), 8.11 (s, 8H, thiophene-H), 7.66 (t, $J = 1.8$ Hz, 4H, *Ar-p*-H), 7.60 (t, $J = 1.8$ Hz, 8H, *Ar-p*-H), 1.42 (s, 72H, *tert*-butyl), and 1.29 (s, 144H, *tert*-butyl) ppm; UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon [M^{-1} cm^{-1}]$) = 437 (300000), 545 (67000), and 578 (50000) nm; HR-MS (MALDI-TOF-MS): $m/z = 4047.84$, calcd for $C_{264}H_{288}N_{16}Ni_4S_4 = 4047.94 [M]^+$.

Synthesis of 4Zn: **4H** (5.0 mg) was added to a round-bottomed 50-mL flask and dissolved in chloroform. An excess amount of saturated zinc(II) acetate in methanol was added. The complete metalation was confirmed by TLC and MALDI-TOF mass spectra. The reaction mixture was passed through a short alumina column and recrystallized with $CH_2Cl_2/MeOH$. **4Zn** was obtained as a red solid quantitatively. **4Zn:** 1H NMR ($CDCl_3$, rt): δ 11.37 (s, 4H, *meso*-H), 9.16 (s, 8H, β -H), 8.93 (d, $J = 5.0$ Hz, 8H, β -H), 8.89 (d, $J = 5.0$ Hz, 8H, β -H), 8.67 (s, 8H, thiophene-H), 8.07 (t, $J = 1.8$ Hz, 8H, *Ar-o*-H), 8.05 (t, $J = 1.8$ Hz, 4H, *Ar-o*-H), 7.98 (t, $J = 1.8$ Hz, 8H, *Ar-o*-H), 7.91 (t, $J = 1.8$ Hz, 4H, *Ar-o*-H), 7.73 (t, $J = 1.8$ Hz, 4H, *Ar-p*-H), 7.71 (t, $J = 1.8$ Hz, 8H, *Ar-p*-H), 1.52 (s, 72H, *tert*-butyl), 1.49 (s, 36H, *tert*-butyl), 1.43 (s, 36H, *tert*-butyl), and 1.37 (s, 72H, *tert*-butyl) ppm; UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon [M^{-1} cm^{-1}]$) = 429 (290000), 452 (270000), 563 (80000), and 597(2600) nm; MS (MALDI-TOF-MS): $m/z = 4074.80$, calcd for $C_{264}H_{288}N_{16}Zn_4S_4 = 4074.90 [M]^+$; Fluorescence (CH_2Cl_2 , $\lambda_{ex} = 428$ nm): $\lambda_{max} = 663$ nm. $\Phi_F = 0.037$.

Single crystals of **4Zn** suitable for X-ray crystallographic analysis were obtained by vapor diffusion of ethanol into toluene and pyridine solution of **4Zn**.

Single crystals of **4Ni**-C₆₀ suitable for X-ray crystallographic analysis were obtained by vapor diffusion of 2-propanol into dichlorobenzene solution of **4Ni** and C₆₀ (the amount of C₆₀ is excess relative to **4Ni**).

MALDI-TOF mass spectra

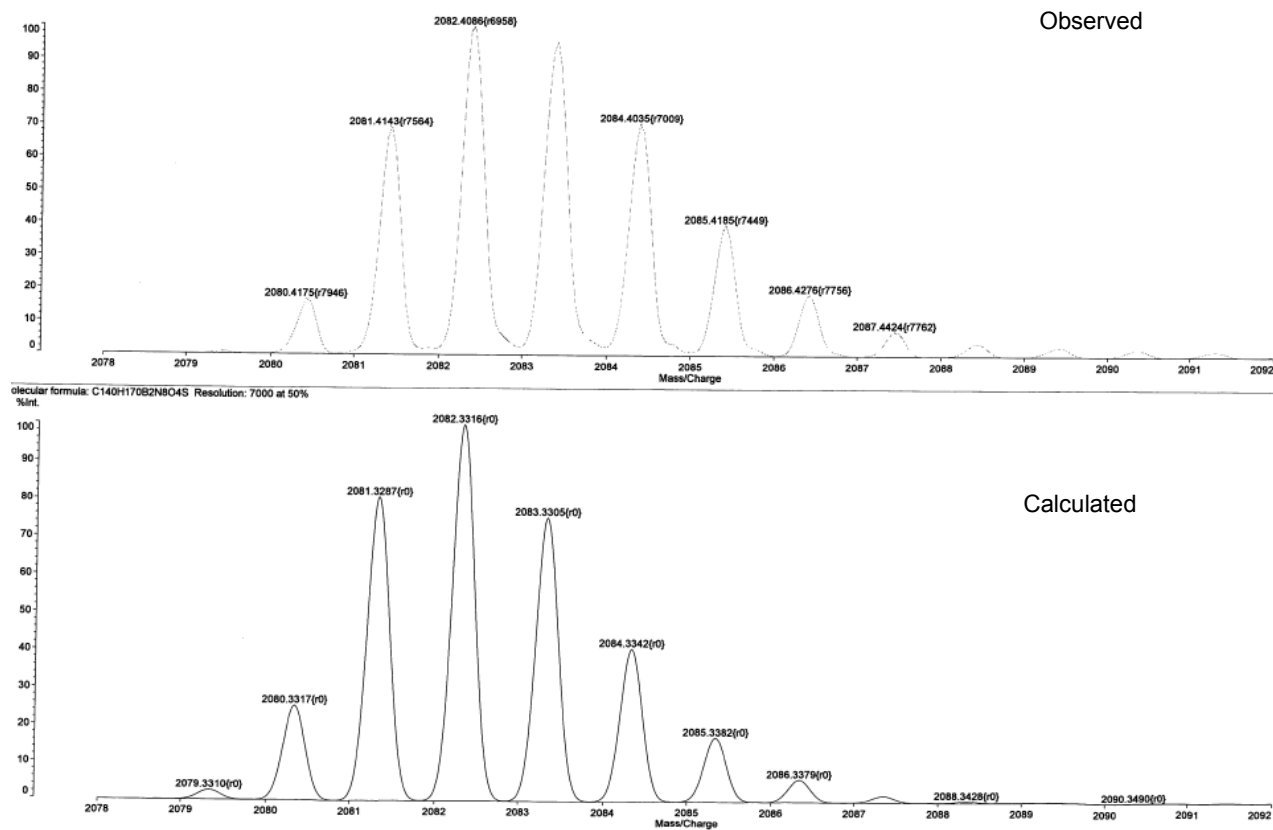
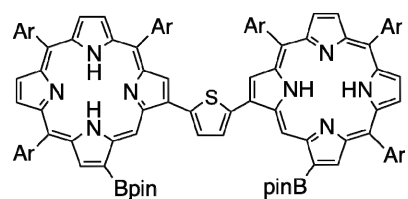


Figure S1. MALDI-TOF mass spectrum of 2B.

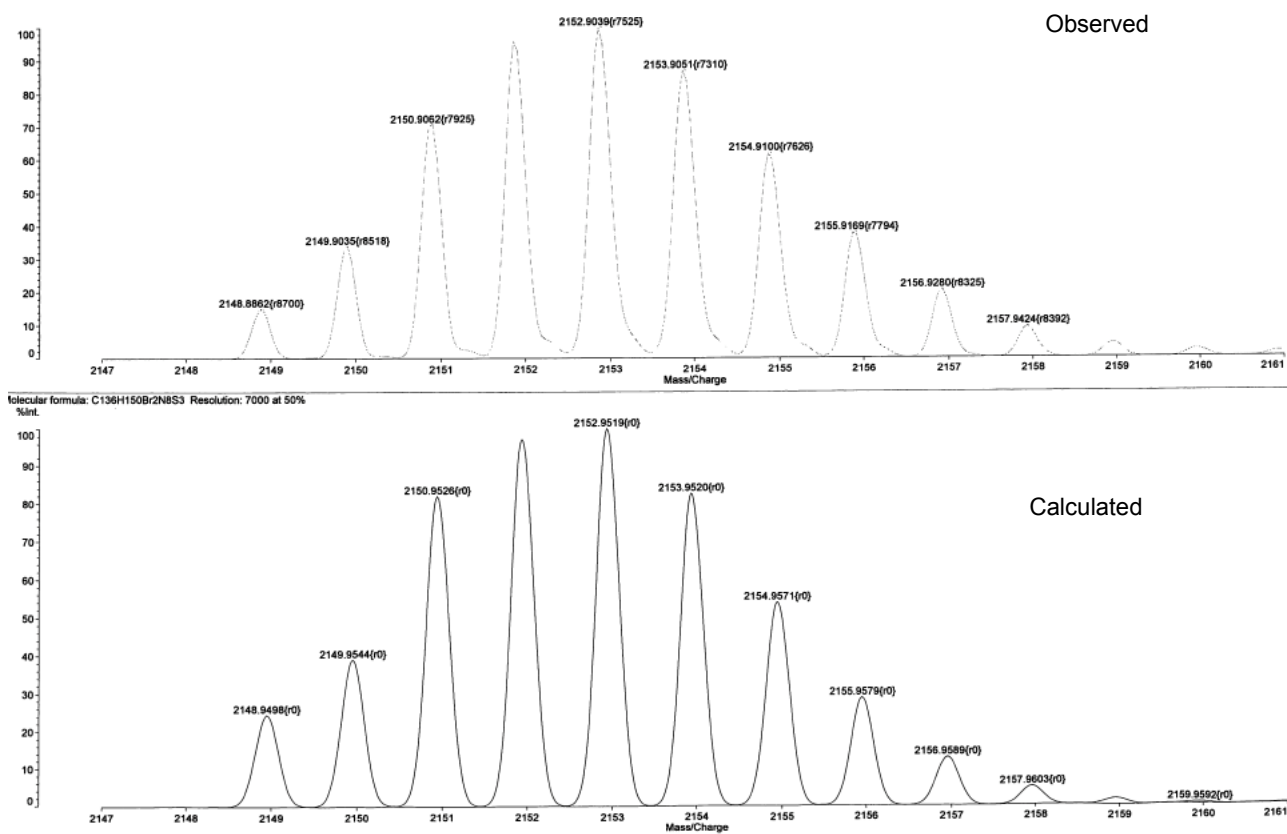
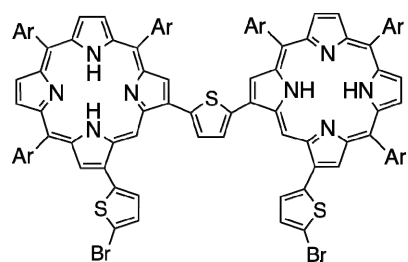


Figure S2. MALDI-TOF mass spectrum of **2Br**.

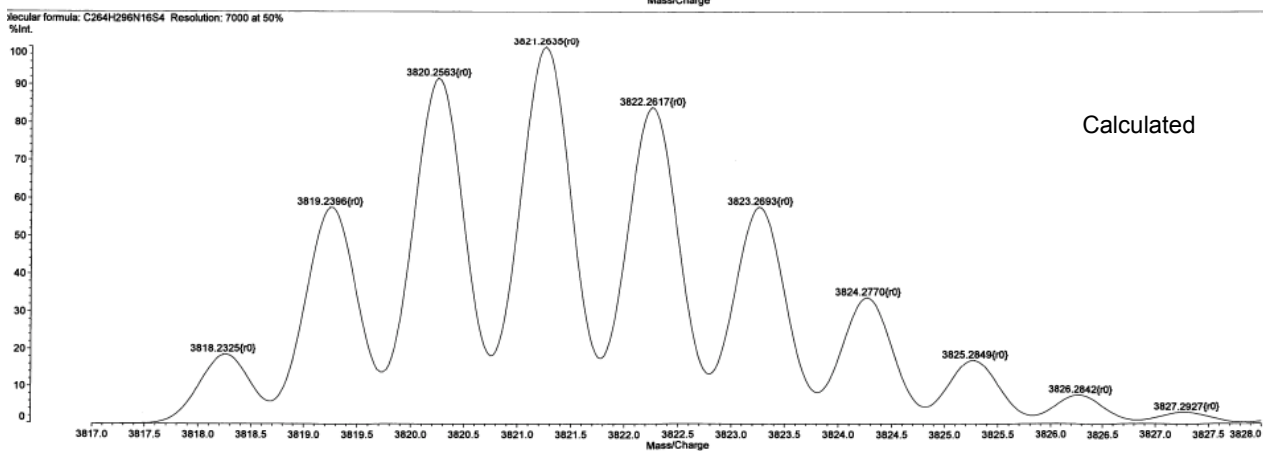
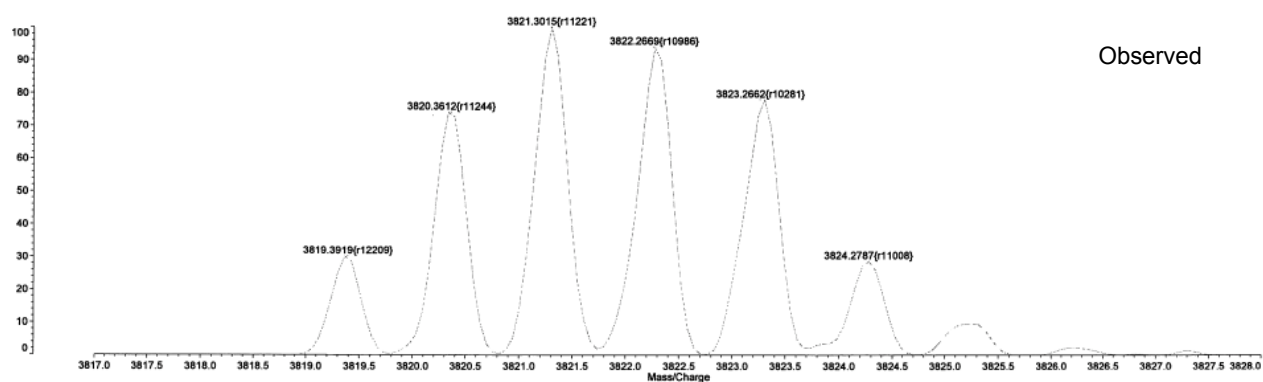
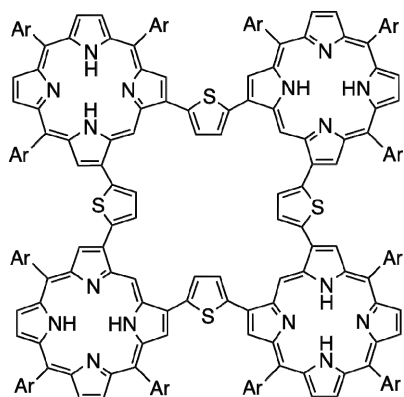


Figure S3. MALDI-TOF mass spectrum of **4H**.

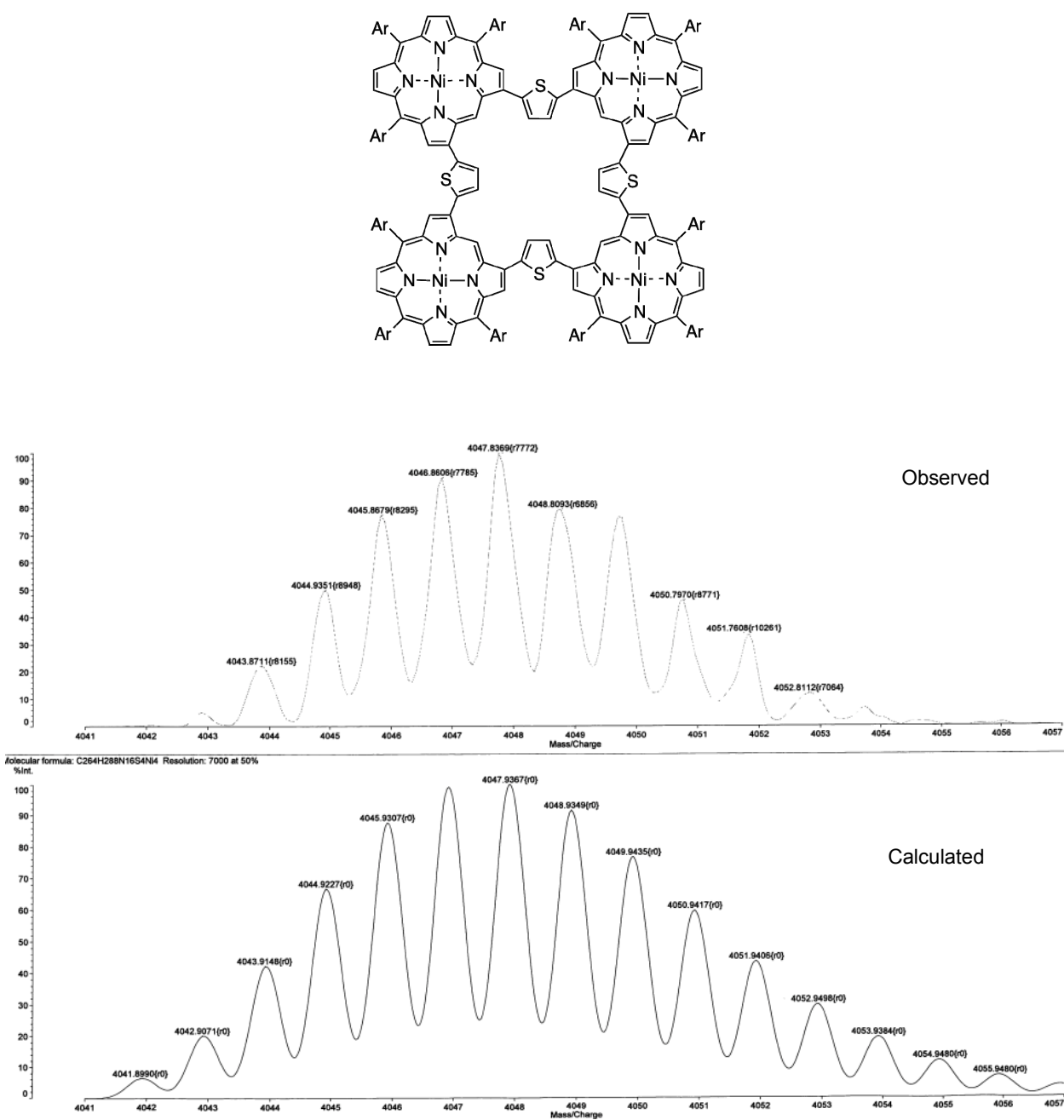


Figure S4. MALDI-TOF mass spectrum of **4Ni**.

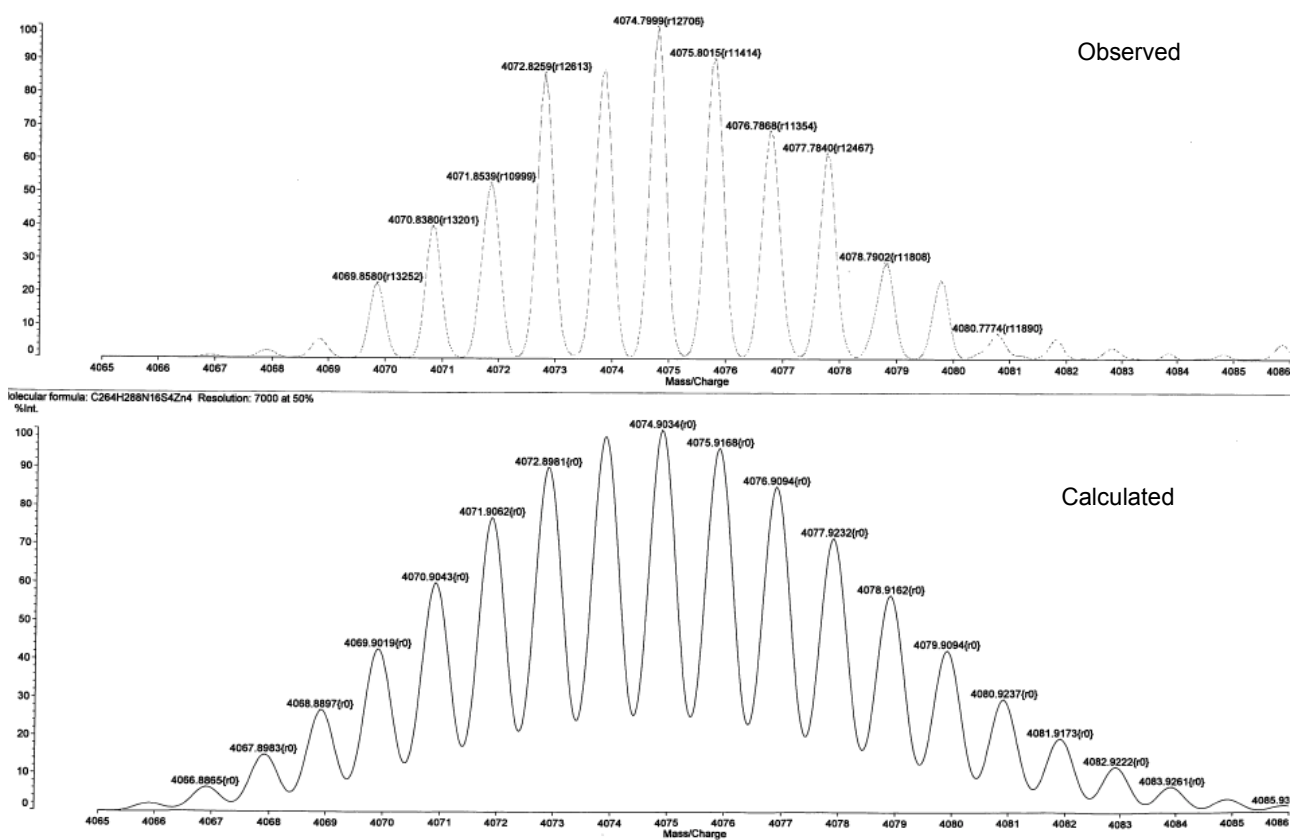
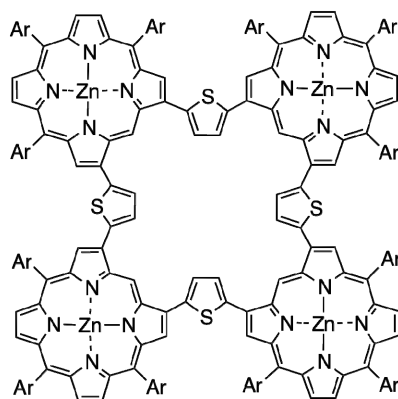


Figure S5. MALDI-TOF mass spectrum of **4Zn**.

^1H NMR spectra

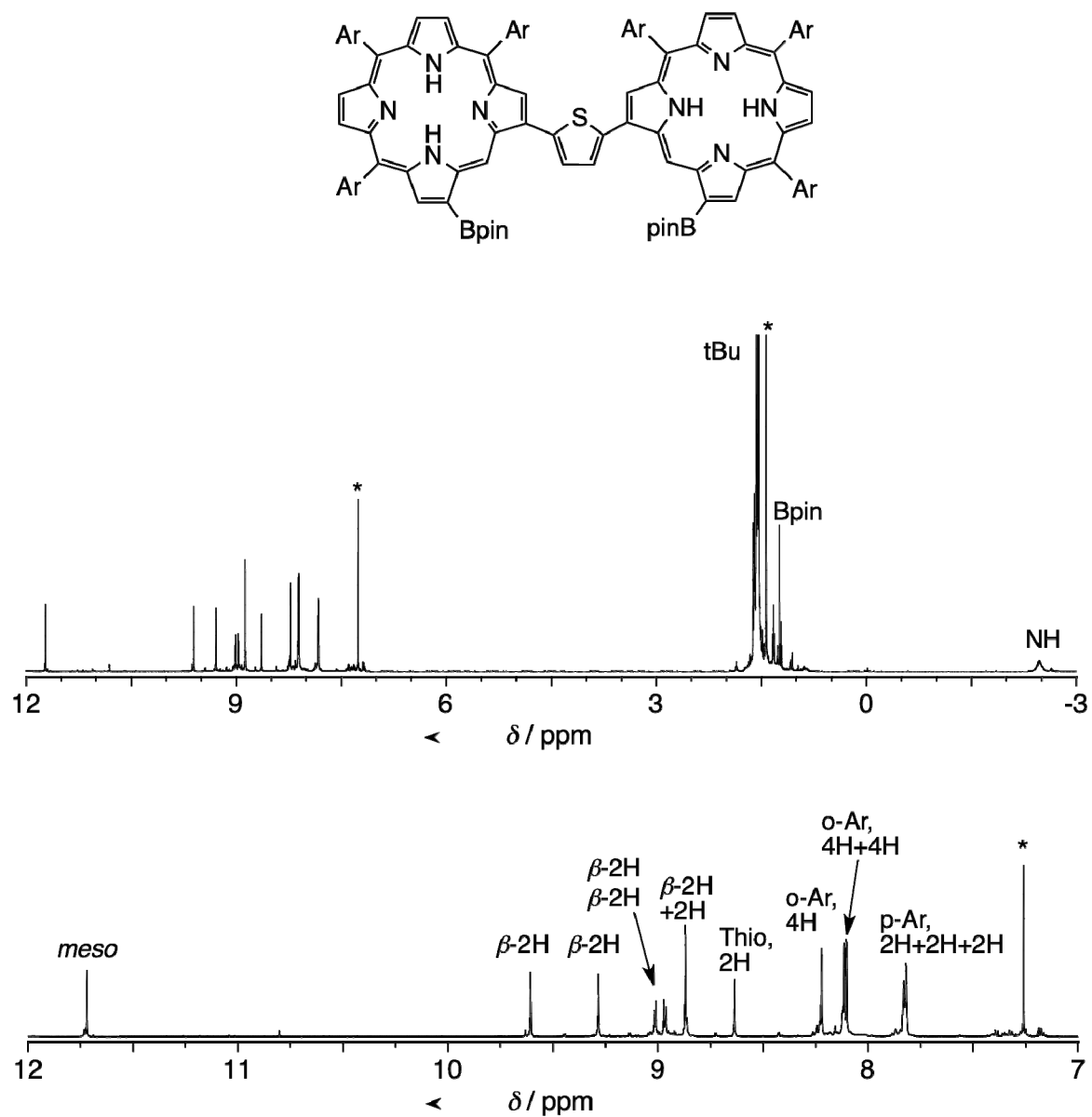


Figure S6. ^1H NMR spectrum of **2B** in CDCl_3 .

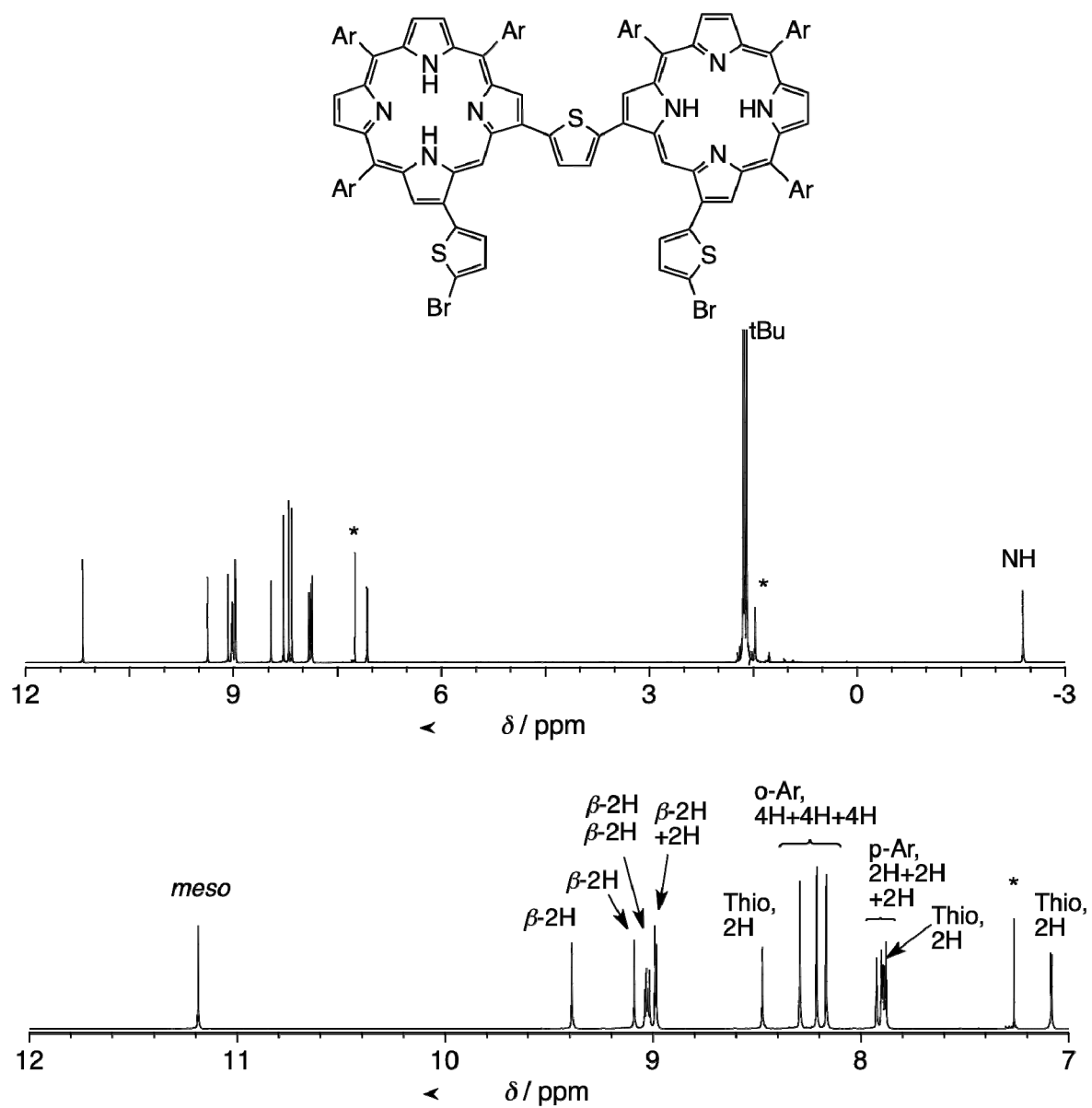


Figure S7. ^1H NMR spectrum of **2Br** in CDCl_3 .

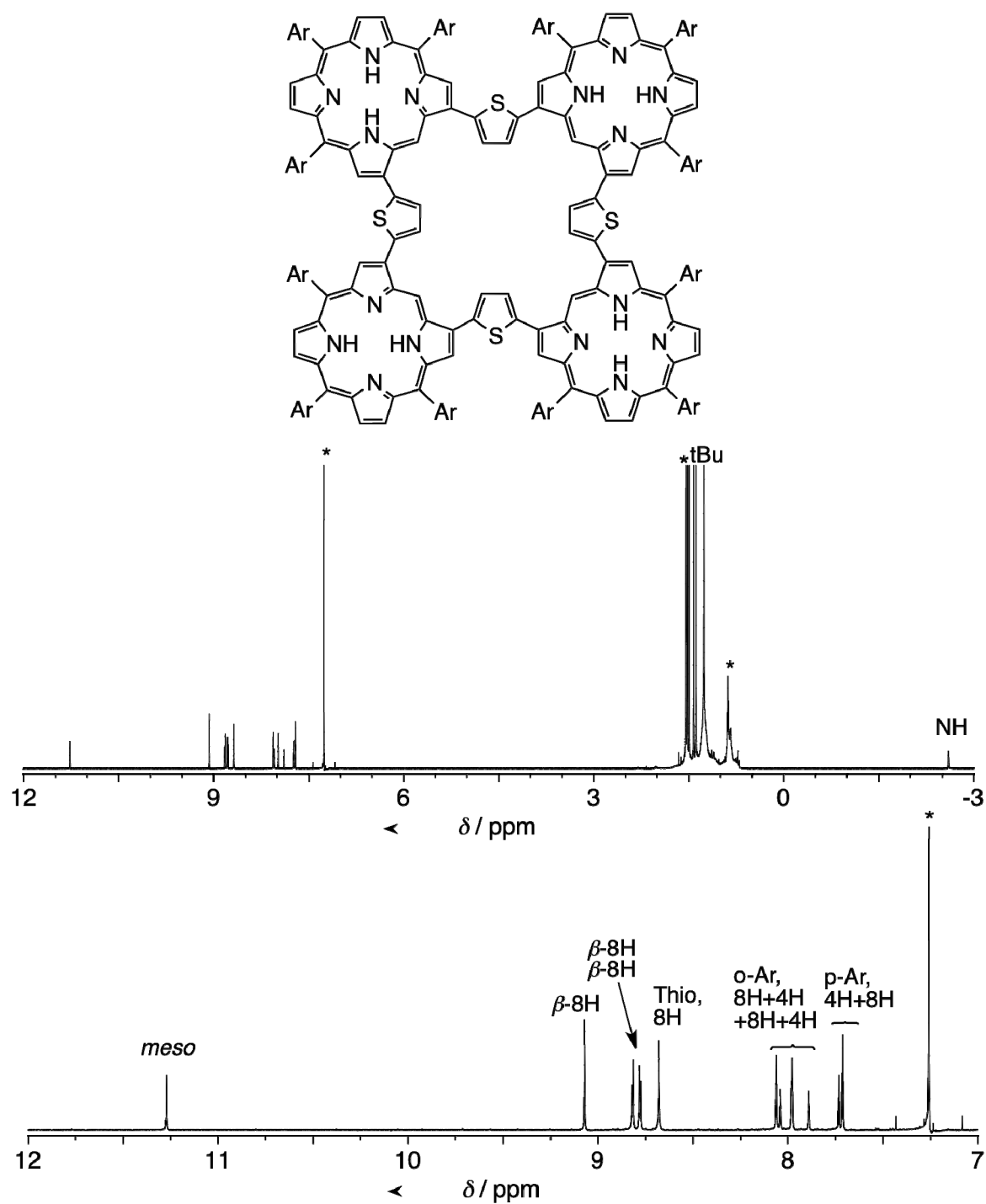


Figure S8. ¹H NMR spectrum of **4H** in CDCl₃.

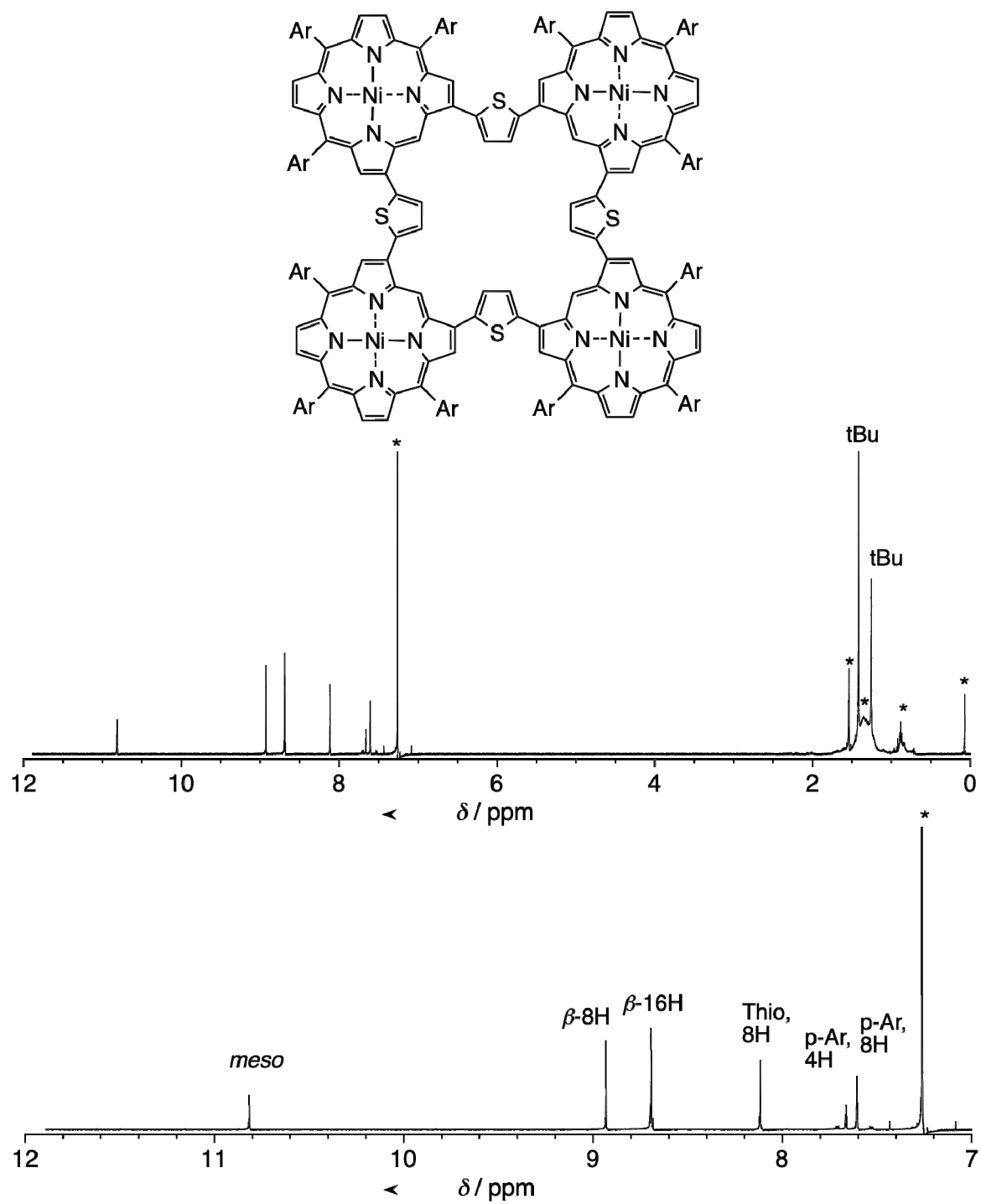


Figure S9. ¹H NMR spectrum of 4Ni in CDCl₃.

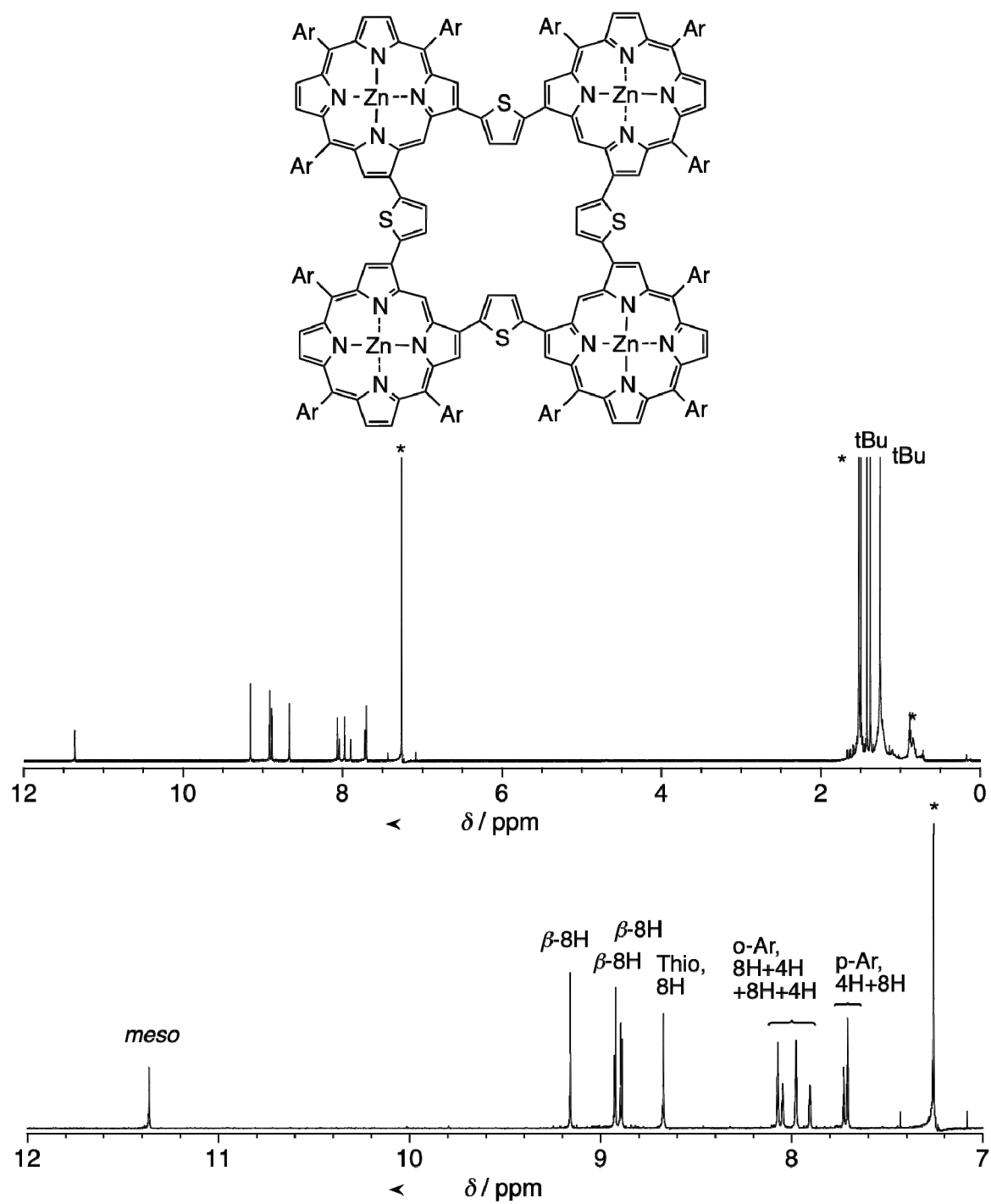


Figure S10. ^1H NMR spectrum of **4Zn** in CDCl_3 .

UV-vis Absorption Spectra

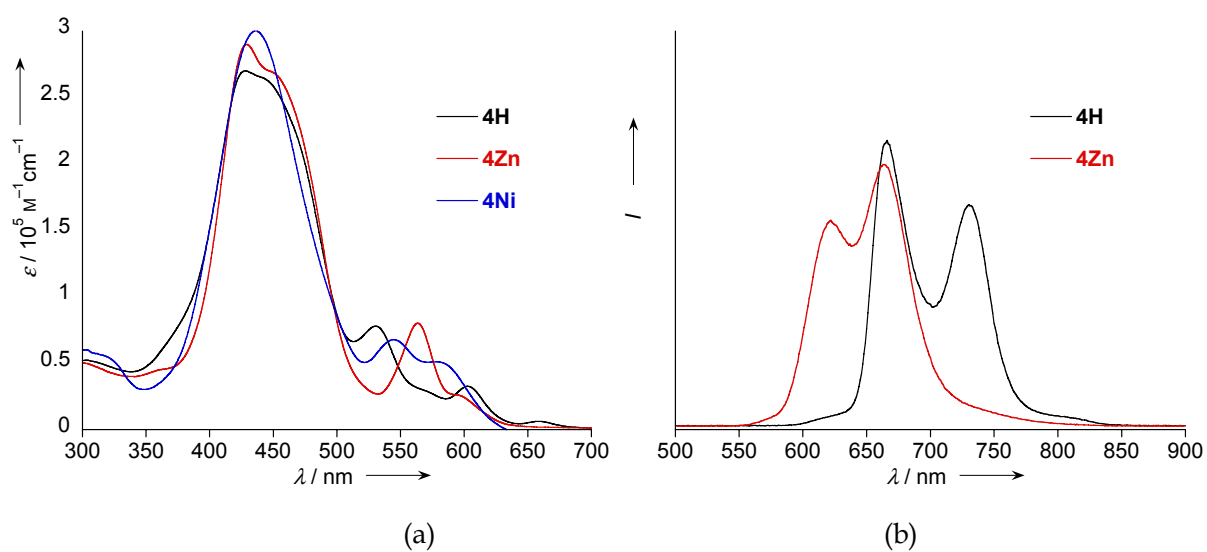


Figure S11. UV-vis absorption spectra of (a) **4H** (black line), **4Zn** (red line), **4Ni** (blue line), and Fluorescence spectra of (b) **4H** (black line), **4Zn** (red line) in dichloromethane.

UV-vis., and ^1H NMR studies of 4Ni with C_{60} and job's plot

Typical procedure of UV-vis. titration

An aliquot of a solution of C_{60} (3.2×10^{-3} M in toluene) was added to a solution of 4Ni (2.0×10^{-6} M in toluene), and the resulting solutions were subjected to UV-vis. spectroscopy at 25°C (Figure S12). The spectrum was corrected with a dilution factor and background subtraction. The difference in absorbance of 4Ni induced by the addition of C_{60} was measured at 438 nm. Binding curves were obtained by plotting y against C_{60} , where y denotes a fraction of complex $4\text{Ni}-\text{C}_{60}$ and defined as $y = (\text{Abs}_{\text{obs}} - \text{Abs}_0) / (\text{Abs}_\infty - \text{Abs}_0)$ where Abs_0 , Abs_∞ is Abs_{obs} at $\text{C}_{60} = 0$ and infinite, respectively (Figure S12, inset). The analysis of the spectral data provided a value of $\log K = 7.7 \pm 0.6$, $N = 1.6$.

Typical procedure of job's plot

Solution of 4Ni and C_{60} (each 0.02 mM in toluene) were mixed to prepare 12 samples (each 0.3 mL) with varying mole fractions of 4Ni from 0 to 1, which were subjected to UV-vis spectroscopies at 25°C . Absorbance values at 438 nm were normalized to the maximal increase ΔAbs in absorbance with the following equation, $\Delta\text{Abs} = \text{Abs}_{\text{obs}} - \text{Abs}_{\text{ref}}$, where Abs_{ref} is absorbance of 4Ni in the absence of C_{60} under the same concentration of 4Ni in the conditions of Abs_{obs} . Job's plot was obtained by plotting ΔAbs values against mole fractions of 4Ni (Figure S13).

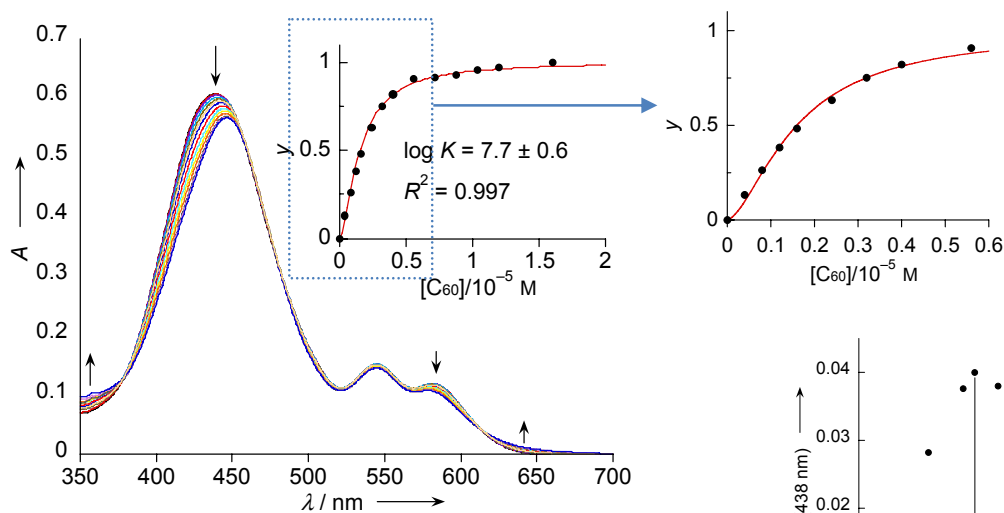


Figure S12. Concentration dependence of the UV-vis absorption spectra: $[4\text{Ni}] = 2.0 \mu\text{M}$, $[\text{C}_{60}] = 0\text{--}16 \mu\text{M}$, toluene, 25°C . formation. Inset: a titration curve of 4Ni under various concentration of $[\text{C}_{60}]$. Low concentration area is enlarged at right side.

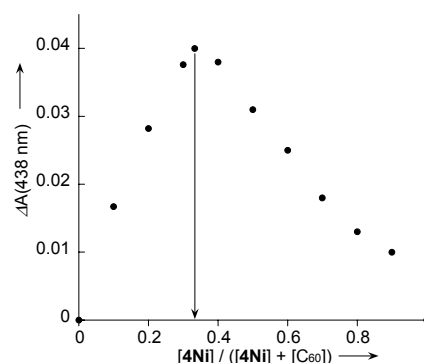


Figure S13. Job's plot for $4\text{Ni}-\text{C}_{60}$ complex formation

Typical procedure of the ^1H NMR titration

An aliquot of a solution of C_{60} was added to a solution of 4Ni , after evaporation and dissolved in suitable CDCl_3 , and the resulting solutions were subjected to ^1H NMR spectroscopy at 25°C (Figure S14).

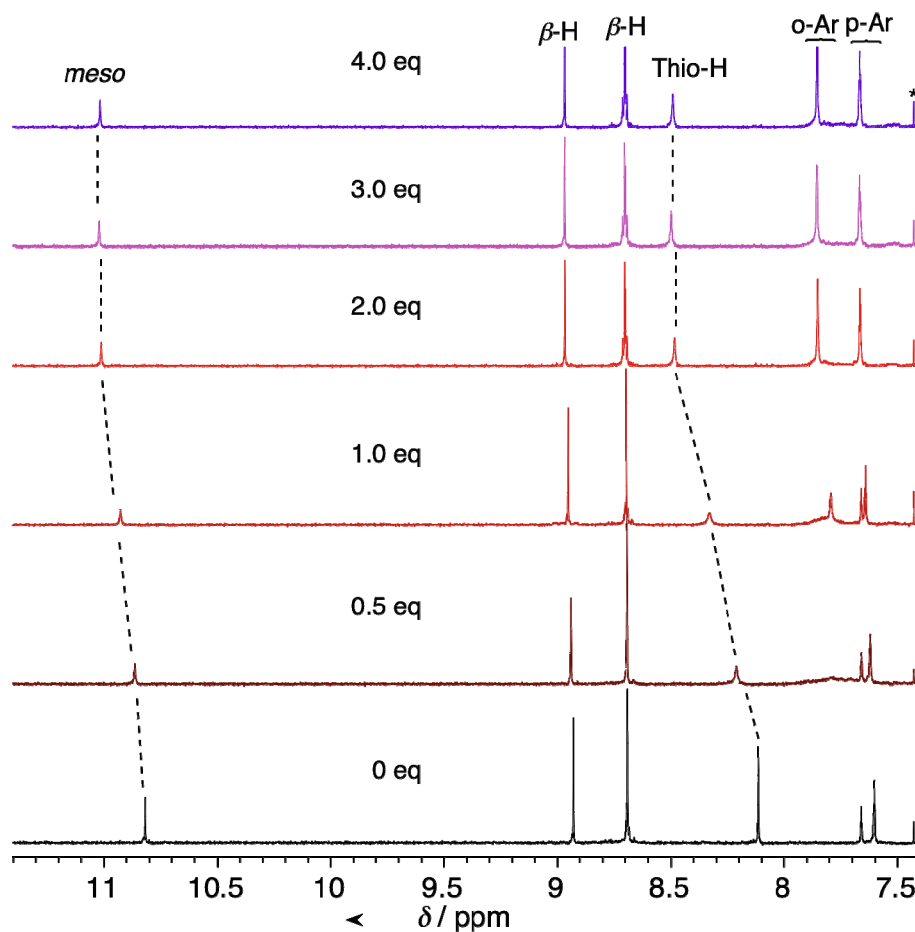


Figure S14 ^1H NMR titration spectra of 4Ni with C_{60} in CDCl_3 at 25°C .

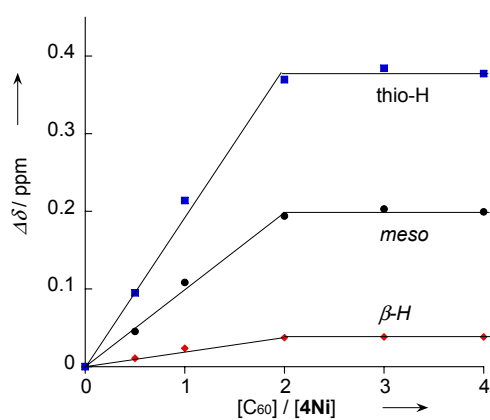


Figure S15. Plots of chemical shift change versus $[\text{C}_{60}]/[4\text{Ni}]$ in CDCl_3 , 25°C . ($\Delta\delta = \delta_{\text{obs}} - \delta_0$, where δ_0 is δ_{obs} at $[\text{C}_{60}] = 0 \text{ M}$)

Table S1. Crystal data for **4Zn** and **4Ni-C₆₀**.

Compound	4Zn*	4Ni-C₆₀*
Empirical formula	C ₂₆₄ H ₂₈₈ N ₁₆ Zn ₄ S ₄	C ₂₆₄ H ₂₈₂ N ₁₆ Ni ₄ S ₄ (C ₆₀) ₃ (dichlorobenzene) ₄
Formula weight	4074.82	6791.90
Temperature (K)	90(2)	90(2)
Wavelength (Å)	0.71069	0.71073
Crystal system	Tetragonal	Monoclinic
Space group	<i>I</i> -42 <i>d</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions	<i>a</i> = 41.392(5) Å <i>c</i> = 22.518(5) Å	<i>a</i> = 25.617(4) Å <i>b</i> = 71.860(12) Å <i>β</i> = 92.466(4)° <i>c</i> = 26.909(5) Å
Volume (Å ³)	38580(11)	49490(14)
Z	4	4
Density (calc) (Mg/m ³)	0.702	0.912
μ (mm ⁻¹)	0.302	0.256
F(000)	8672	14120
Crystal size (mm ³)	0.60 × 0.30 × 0.20	0.30 × 0.20 × 0.10
θ for data collection	1.39 to 23.50°	0.84 to 23.50°
Index ranges	-46 ≤ <i>h</i> ≤ 42, -46 ≤ <i>k</i> ≤ 45, -25 ≤ <i>l</i> ≤ 23	-28 ≤ <i>h</i> ≤ 28, -79 ≤ <i>k</i> ≤ 80, -25 ≤ <i>l</i> ≤ 30
Reflections collected	87359	113582
Independent reflections	14251 [<i>R</i> (int) = 0.1355]	36533 [<i>R</i> (int) = 0.1018]
Completeness	99.7 % (θ = 23.50°)	99.7 % (θ = 23.50°)
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.9421 and 0.8397	0.9748 and 0.9271
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	14251 / 604 / 613	36533 / 3447 / 2999
Goodness-of-fit on <i>F</i> ²	0.715	0.991
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0860, <i>wR</i> ₂ = 0.2110	<i>R</i> ₁ = 0.1191, <i>wR</i> ₂ = 0.2915
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2196, <i>wR</i> ₂ = 0.2413	<i>R</i> ₁ = 0.1780, <i>wR</i> ₂ = 0.3194
Largest diff. peak and hole	0.252 and -0.238 e.Å ⁻³	0.929 and -0.361 e.Å ⁻³
CCDC number	801517	801516

* The contributions to the scattering arising from the presence of the disordered solvents in the crystal were removed by use of the utility SQUEEZE in the PLATON software package.

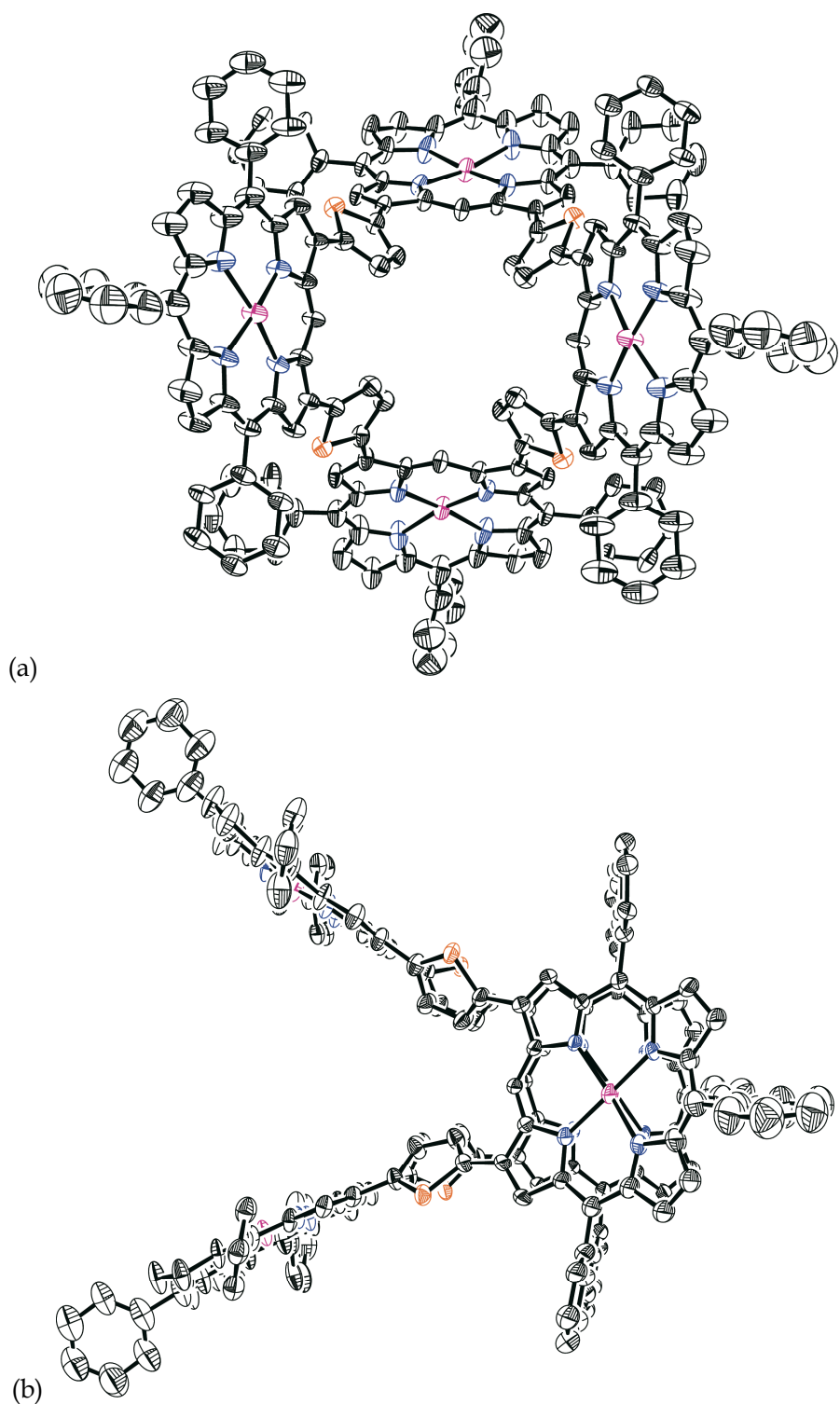


Figure S16. X-Ray crystal structure of **4Zn**. (a) Top view, and (b) side view. The thermal ellipsoids are 15% probability level. Hydrogen atoms and ^tBu groups are omitted for clarity.

Explanation for a "level A" alert: Since the crystals contained many severely disordered solvent molecules, they gave only weak diffractions. However, these are not significant concern for the main skeletal structure.

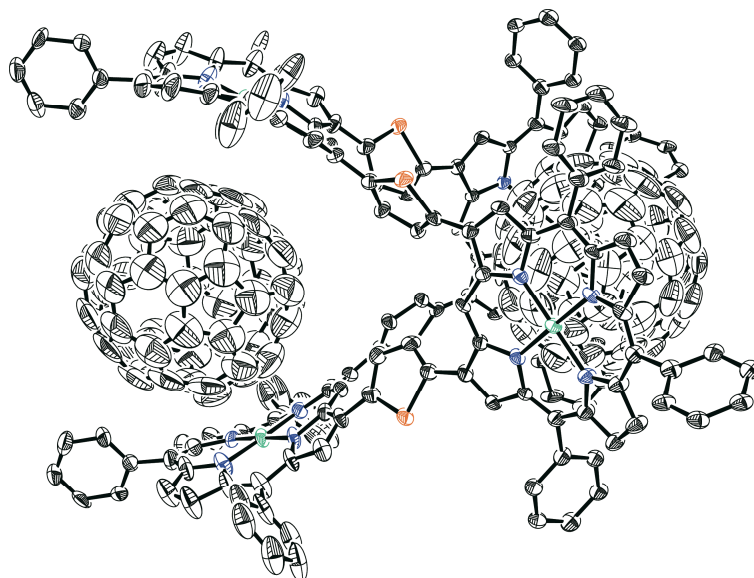


Figure S17. X-Ray crystal structure of 4Ni-C_{60} . The thermal ellipsoids are 30% probability level. Hydrogen atoms, solvent molecules, disordered and outside C_{60} molecules, and $t\text{-Bu}$ groups are omitted for clarity.

Explanation for a "level A" alert: The alert comes from the rotational disorder of *tert*-Butyl groups.

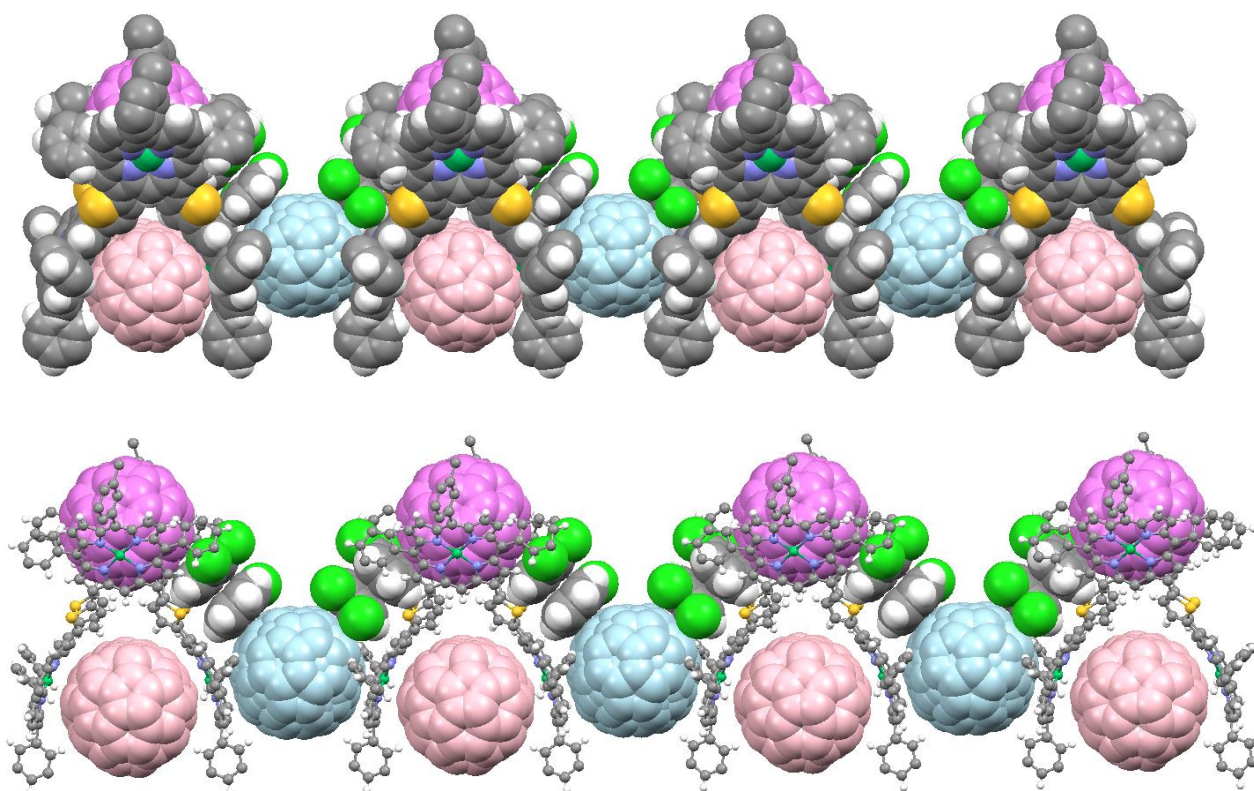


Figure S18. A columnar zigzag array of the fullerene molecules along the a -axis shown as a space-filling model. The blue fullerene molecules interconnect face-to-face with two $(\text{C}_{60})_2@4\text{Ni}$. For clarity, 4Ni units at bottom are shown as a ball-and-stick model. $t\text{-Bu}$ groups are omitted for clarity.