

Supplementary Information

Synthesis of thiophene-fused porphyrin dimers as efficiently π -extended helical chromophores

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1. Experimental Section

Instrumentation and Materials.

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Silica-gel column chromatography was performed with UltraPure Silica Gel (230-400 mesh, SiliCycle) unless otherwise noted. Thin-layer chromatography (TLC) was performed with Silica gel 60 F₂₅₄ (Merck). UV/Vis/NIR absorption spectra were measured with a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. ¹H, and ¹³C spectra were recorded with a JEOL EX-400 spectrometer (operating at 399.65 MHz for ¹H and 100.40 MHz for ¹³C) by using the residual solvent as the internal reference for ¹H (CDCl₃: δ = 7.26 ppm; toluene-*d*₈: δ = 2.08 ppm; C₂D₂Cl₄: δ = 6.00 ppm) and ¹³C (CDCl₃: δ = 77.16 ppm). High-resolution mass spectra (HRMS) were measured on a Thermo Fischer Scientific EXACTIVE Fourier-transform orbitrap mass spectrometer (APCI). Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were taken with the golden gate diamond anvil ATR accessory (NICOLET 6700, Thermo scientific), using typically 64 scans at a resolution of 2 cm⁻¹. All samples were placed in contact with the diamond window using the same mechanical force. Single crystal X-ray diffraction analysis data for **1a** were collected at monochromated MoK α radiation (0.71075 Å). The structures were solved by direct method (SHELXS-2014). Redox potentials were measured by cyclic voltammetry and differential pulse voltammetry method on an ALS electrochemical analyzer model 660A.

Density Functional Theory (DFT) Calculations.

All calculations were carried out using the *Gaussian 09* program.^{S1} The calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) level,^{S2,S3} employing a basis set 6-31G(d,p) for C, H, N, O, S, Ni, and Zn.

2. Synthesis

[3-Iodo-5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrinato]nickel(II) (**3a**)^{S4}, [3-iodo-5,15-bis(3,5-di-*tert*-butylphenyl)-10-(2,4,6-trimethylphenyl)porphyrinato]nickel(II) (**3b**)^{S5}, and 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (**4**)^{S6} were prepared according to literatures.

Thiophene-bridged porphyrin dimer (5a): A flask containing **3a** (211 mg, 0.2 mmol), thiophene **4** (33.6 mg, 0.1 mmol), SPhos-Pd-G2 (7.2 mg, 0.01 mmol) and K₃PO₄ (106 mg, 0.5 mmol) was purged with argon, and charged with THF (8 mL) and H₂O (2 mL). After stirring for 3 h at 65 °C, the reaction mixture was cooled to room temperature, quenched with water, extracted with CH₂Cl₂, and dried over Na₂SO₄. After removal of solvent, the crude product was purified with silica gel column chromatography using a 8:1 mixture of *n*-hexane and CH₂Cl₂ to afford **5a**. Reprecipitation from CH₂Cl₂ and MeOH gave **5a** (128.9 mg, 0.0663 mmol, 66%) as a red solid.

5a:^{S7} ¹H NMR (399.65 MHz, CDCl₃, 25 °C): δ = 10.36 (s, 2H, *meso*), 9.20 (d, *J* = 4.3 Hz, 2H, β), 9.14 (s, 2H, β), 8.95 (d, *J* = 4.9 Hz, 2H, β), 8.50-8.83 (m, 8H, β), 8.14 (s, 2H, Thieryl), 7.98 (d, *J* = 1.8 Hz, 4H, Ar-*ortho*), 7.91 (d, *J* = 1.8 Hz, 4H, Ar-*ortho*), 7.89 (d, *J* = 1.8 Hz, 4H, Ar-*ortho*), 7.78-7.77 (m, 2H, Ar-*para*), 7.75-7.74 (m, 2H, Ar-*para*), 7.72 (m, 2H, Ar-*para*), 1.52 (s, 36H, *tert*-Butyl), 1.50 (s, 36H, *tert*-Butyl), 1.48 (s, 36H, *tert*-Butyl) ppm.

Thiophene-bridged porphyrin dimer (5b): A flask containing **3b** (41.7 mg, 0.042 mmol), thiophene **4** (7.09 mg, 0.021 mmol), SPhos-Pd-G2 (1.5 mg, 0.0021 mmol) and K₃PO₄ (22.3 mg, 0.11 mmol) was purged with argon, and charged with THF (1.6 mL) and H₂O (0.4 mL). After stirring for 13 h at 65 °C, the reaction mixture was cooled to room temperature, quenched with water, extracted with CH₂Cl₂, and dried over Na₂SO₄. After removal of solvent, the crude product was purified with silica gel column chromatography using a 6:1 mixture of *n*-hexane and CH₂Cl₂. Reprecipitation from CH₂Cl₂ and MeOH gave **5b** (26.6 mg, 0.0147 mmol, 70%) as a red solid.

5b: ¹H NMR (399.65 MHz, CDCl₃, 25 °C): δ = 10.36 (s, 2H, *meso*), 9.20 (d, *J* = 4.9 Hz, 2H, β), 9.13 (s, 2H, β), 8.94 (d, *J* = 4.9 Hz, 2H, β), 8.84 (d, *J* = 4.9 Hz, 2H, β), 8.81 (d, *J* = 4.9 Hz, 2H, β), 8.63 (d, *J* = 4.9 Hz, 4H, β), 8.13 (s, 2H, Thieryl), 7.99 (d, *J* = 1.8 Hz, 4H, Ar-*ortho*), 7.93 (d, *J* = 1.8 Hz, 4H, Ar-*ortho*), 7.77 (m, 2H, Ar-*para*), 7.75 (m, 2H, Ar-*para*), 7.21 (s, 4H, Mes), 2.57 (s, 6H, Methyl), 1.84 (s, 12H, Methyl), 1.53 (s, 36H, *tert*-Butyl), 1.50 (s, 36H, *tert*-Butyl) ppm. ¹³C NMR (100.40 MHz, CDCl₃, 25 °C): δ = 149.3, 149.2, 143.5, 143.4, 143.3, 143.2, 142.7, 142.6, 141.7, 140.1, 140.0, 139.8, 139.1, 137.8, 137.6, 137.5, 133.1, 133.0, 132.4, 131.4, 131.3, 130.7, 129.5, 129.3, 129.1, 127.9, 121.33, 121.29, 120.2, 119.9, 117.7, 104.2, 35.23, 35.19, 31.90, 31.87, 21.59, 21.55 ppm. HRMS (APCI) calcd for C₁₁₈H₁₂₄N₈Ni₂S₁; [M+H]⁺: 1801.8449;

found 1801.8446. FT-IR (ATR): $\nu = 2953, 2867, 1592, 1461, 1427, 1382, 1362, 1334, 1298, 1246, 1202, 1069, 1001, 974, 928, 900, 883, 827, 814, 796, 714 \text{ cm}^{-1}$. m.p.: $> 300 \text{ }^\circ\text{C}$.

Thiophene-fused helical porphyrin dimer (1a): A flask containing **5a** (100 mg, 0.0514 mmol) was purged with argon, and then charged with CHCl_3 (10.3 mL). Palau'Chlor (23.7 mg, 0.113 mmol) was added to the mixture at $0 \text{ }^\circ\text{C}$. The reaction mixture was stirred at $0 \text{ }^\circ\text{C}$ for 30 min, and then stirred at room temperature for 13 h. The mixture was diluted with CH_2Cl_2 , and then filtered through a small plug of silica gel with copious washing with CH_2Cl_2 . After removal of solvent, the crude product of **6a** was using for next step without further purification. A flask containing **6a**, $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.0103 mmol), $\text{PCy}_3 \cdot \text{HBF}_4$ (7.6 mg, 0.0206 mmol), and K_2CO_3 (14.2 mg, 0.103 mmol) was purged with argon, and charged with DMF (2.6 mL). The mixture was heated to reflux with stirring for 3.5 h, and then cooled to ambient temperature. The mixture was extracted with toluene, and dried over Na_2SO_4 . After removal of solvent, the crude product was purified with silica gel column chromatography using a 10:1 mixture of *n*-hexane and CH_2Cl_2 to afforded **1a**. Recrystallization from CH_2Cl_2 and MeOH gave **1a** (43.4 mg, 0.0224 mmol, 43%) as a dark solid.

1a: ^1H NMR (399.65 MHz, CDCl_3 , $25 \text{ }^\circ\text{C}$): $\delta = 8.33$ (d, $J = 5.4 \text{ Hz}$, 2H, β), 8.22-8.07 (m, 14H, $\beta + \text{Ar-ortho}$), 7.65 (m, 4H, *Ar-para*), 7.55 (m, 2H, *Ar-para*), 7.35 (s, 2H, β), 7.22 (br, 4H, *Ar-ortho*), 7.01 (br, 4H, *Ar-ortho*), 1.56-1.23 (m, 108H, *tert*-Butyl) ppm. ^{13}C NMR (100.40 MHz, CDCl_3 , $25 \text{ }^\circ\text{C}$): $\delta = 158.6, 149.7, 149.41, 149.37, 149.3, 146.9, 145.9, 145.3, 144.8, 143.2, 143.0, 142.9, 141.0, 140.9, 139.2, 139.1, 138.0, 133.8, 133.4, 131.3, 130.7, 129.9, 129.7, 128.7, 128.0, 125.9, 125.7, 121.6, 121.4, 121.1, 120.4, 119.9, 109.3, 35.1, 31.8$ ppm. UV/Vis/NIR (CH_2Cl_2): λ (ϵ , $\text{M}^{-1} \cdot \text{cm}^{-1}$) = 426 (139000), 462 (93200), 557 (49000), 615 (74300), 864 (4600), 975 (2500) nm. HRMS (APCI) calcd for $\text{C}_{128}\text{H}_{140}\text{N}_8\text{Ni}_2\text{S}_1$; $[\text{M}+\text{H}]^+$: 1937.9701; found 1937.9672. FT-IR (ATR): $\nu = 2953, 2904, 2867, 1592, 1461, 1425, 1393, 1361, 1298, 1247, 1072, 1012, 994, 974, 938, 900, 882, 861, 825, 715, 693 \text{ cm}^{-1}$. m.p.: $> 300 \text{ }^\circ\text{C}$.

Thiophene-fused helical porphyrin dimer (1b): A flask containing **5b** (175.7 mg, 0.0974 mmol) was purged with argon, and then charged with CHCl_3 (19.5 mL). Palau'Chlor (44.9 mg, 0.214 mmol) was added to the mixture at $0 \text{ }^\circ\text{C}$. The reaction mixture was stirring at $0 \text{ }^\circ\text{C}$ for 30 min, and then stirred at room temperature for 13 h. The mixture was diluted with CH_2Cl_2 , and then filtered through a small plug of silica gel with copious washing with CH_2Cl_2 . After removal of solvent, the crude product of **6b** was using for next step without further purification. A flask containing **6b**, $\text{Pd}(\text{OAc})_2$ (4.4 mg, 0.0195 mmol), $\text{PCy}_3 \cdot \text{HBF}_4$ (14.3 mg, 0.0390 mmol), and K_2CO_3 (26.9 mg, 0.195 mmol) was purged with argon, and charged with DMF (4.9 mL). The mixture was heated to reflux with stirring

for 4.5 h, and then cooled to ambient temperature. The mixture was extracted with toluene, and dried over Na₂SO₄. After removal of solvent, the crude product was purified with silica gel column chromatography using a 8:1 mixture of *n*-hexane and CH₂Cl₂ to afford **1b**. Recrystallization from CH₂Cl₂ and MeOH gave **1b** (52.7 mg, 0.0293 mmol, 30%) as a dark solid.

1b: ¹H NMR (399.65 MHz, CDCl₃, 25 °C): δ = 8.34 (d, *J* = 4.9 Hz, 2H, β), 8.15-8.00 (m, 12H, β + Ar-ortho), 7.92 (d, *J* = 4.3 Hz, 2H, β), 7.65-7.64 (m, 2H, Ar-para), 7.54-7.53 (m, 2H, Ar-para), 7.33 (s, 2H, β), 7.22 (brs, 2H, Mes), 7.04 (brs, 2H, Mes), 2.50 (s, 6H, Methyl), 2.24 (s, 6H, Methyl), 1.61-1.22 (m, 78H, *tert*-Butyl and Methyl) ppm. ¹³C NMR (100.40 MHz, CDCl₃, 25 °C): δ = 158.6, 149.7, 149.4, 149.3, 147.0, 146.0, 145.4, 144.9, 142.8, 142.7, 142.4, 141.0, 140.9, 139.1, 138.7, 138.6, 138.0, 137.8, 136.3, 133.8, 132.1, 131.8, 131.1, 129.8, 128.8, 128.1, 128.0, 125.5, 122.9, 121.6, 121.1, 120.5, 120.0, 109.5, 35.2, 35.0, 31.9, 31.7, 31.6, 29.9, 21.5, 21.4, 21.0 ppm. UV/Vis/NIR (CH₂Cl₂): λ (ε, M⁻¹·cm⁻¹) = 417 (107000), 458 (90500), 559 (48600), 613 (78100), 859 (4700), 975 (2300) nm. HRMS (APCI) calcd for C₁₁₈H₁₂₀N₈Ni₂Si; [M+H]⁺: 1797.8136; found 1797.8126. FT-IR (ATR): ν = 2951, 2865, 1590, 1458, 1393, 1351, 1296, 1240, 1201, 1069, 1008, 991, 972, 935, 899, 882, 855, 825, 796, 741, 716, 697, 685 cm⁻¹. m.p.: > 300 °C.

Thiophene-fused helical porphyrin dimer (**2**):

Conc. H₂SO₄ (0.22 mL) was added to the mixture of **1b** (40 mg, 0.0222 mmol) and trifluoroacetic acid (2.2 mL) at 0 °C. The reaction mixture was stirring for 2 h at 0 °C under dark condition. After neutralization by KOH aq. at 0 °C, the product was extracted with CH₂Cl₂ and dried over Na₂SO₄. After removal of solvent, a solution of Zn(OAc)₂·2H₂O (97.6 mg, 0.445 mmol) in MeOH (1.1 mL) was added to the crude product in CH₂Cl₂ (1.1 mL). The reaction mixture was stirring for 1h at room temperature under dark condition. After removal of solvent, the mixture was diluted with a 1:1 mixture of *n*-hexane and CH₂Cl₂ and filtered through a small plug of silica gel with copious washings with a 1:1 mixture of *n*-hexane and CH₂Cl₂ as eluent to afford **2** (38.4 mg, 0.0212 mmol, 95%) as a dark solid.

2: ¹H NMR (399.65 MHz, CDCl₃, 25 °C): δ = 8.75 (d, *J* = 4.9 Hz, 2H, β), 8.28 (d, *J* = 4.3 Hz, 2H, β), 8.21 (d, *J* = 4.3 Hz, 2H, β), 8.19 (d, *J* = 4.9 Hz, 2H, β), 8.17 (d, *J* = 4.9 Hz, 2H, β), 8.11 (m, 2H, Ar), 8.08 (m, 2H, Ar), 8.06 (d, *J* = 4.3 Hz, 2H, β), 7.70-7.69 (m, 2H, Ar), 7.67 (m, 2H, Ar), 7.61-7.60 (m, 2H, Ar), 7.56 (m, 2H, Ar), 7.31 (s, 2H, β), 7.21 (brs, 2H, Mes), 7.15 (brs, 2H, Mes), 2.56 (s, 6H, Methyl), 2.05 (s, 6H, Methyl), 1.81 (s, 6H, Methyl), and 1.57 (s, 18H, *tert*-Butyl), 1.50 (s, 18H, *tert*-Butyl), 1.47 (s, 18H, *tert*-Butyl), 1.33 (s, 18H, *tert*-Butyl) ppm. ¹³C NMR (100.40 MHz, CDCl₃, 25 °C): δ = 167.7, 154.3, 153.9, 153.3, 152.4, 151.6, 150.2, 149.2, 149.1, 148.9, 148.5, 142.8, 141.5, 140.8, 139.7, 138.9, 138.7, 138.3, 137.5, 132.4, 131.8, 131.5, 131.3, 130.8, 130.1, 129.6, 129.2, 129.1, 127.9, 127.8, 124.8, 121.8, 121.3, 120.6, 118.3,

112.1, 35.20, 35.15, 35.1, 35.0, 31.94, 31.90, 31.86, 31.7, 29.9, 21.6, 21.5, 21.4 ppm. UV/Vis/NIR (CH₂Cl₂): λ (ϵ , M⁻¹·cm⁻¹) = 422 (113000), 436 (108000), 475 (106000), 568 (45100), 661 (71000), 910 (4000), 1040 (1400) nm. HRMS (APCI) calcd for C₁₁₈H₁₂₀N₈Zn₂S₁; [M+H]⁺: 1809.8012; found 1809.7994. FT-IR (ATR): ν = 2952, 2862, 1589, 1475, 1458, 1424, 1392, 1360, 1335, 1285, 1243, 1200, 1063, 1007, 984, 966, 934, 881, 820, 795, 738, 727, 715 cm⁻¹. m.p.: > 300 °C.

3. High-Resolution Mass Spectra

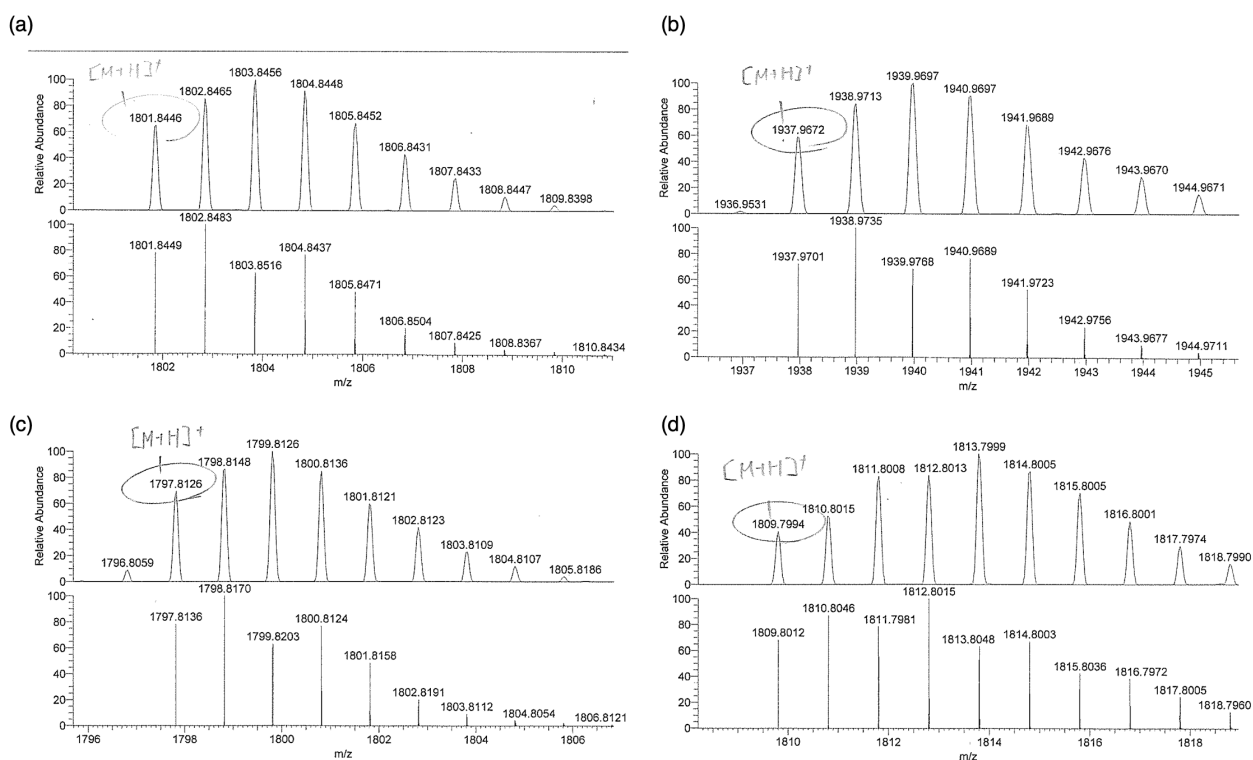


Figure S1. Observed (top) and simulated (bottom) high-resolution mass spectra of (a) **5b**, (b) **1a**, (c) **1b**, and (d) **2**.

4. NMR Spectra

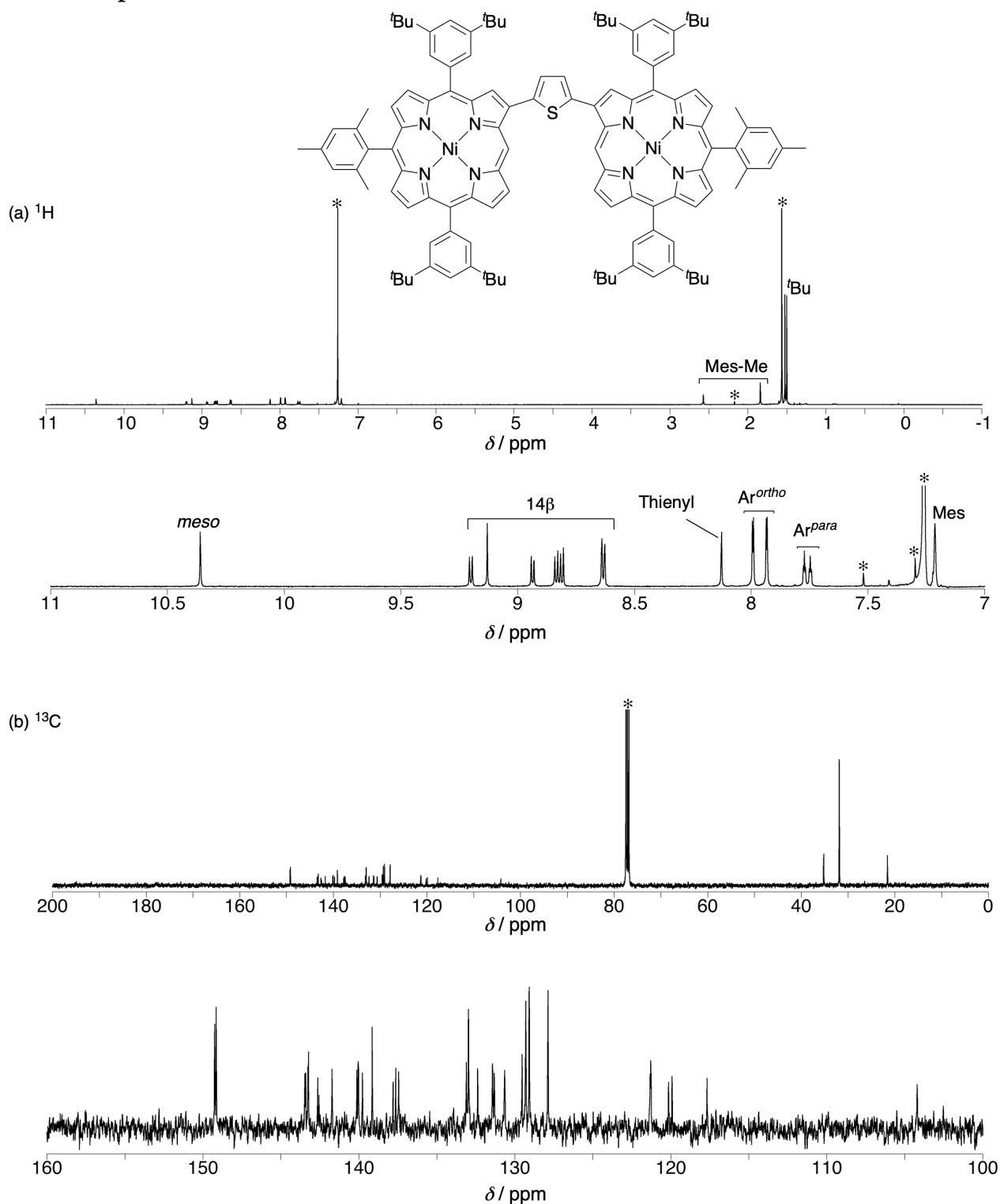


Figure S2. (a) 1H and (b) ^{13}C NMR spectra of **5b** at 25 °C in $CDCl_3$. Peaks marked with * arise from residual solvents.

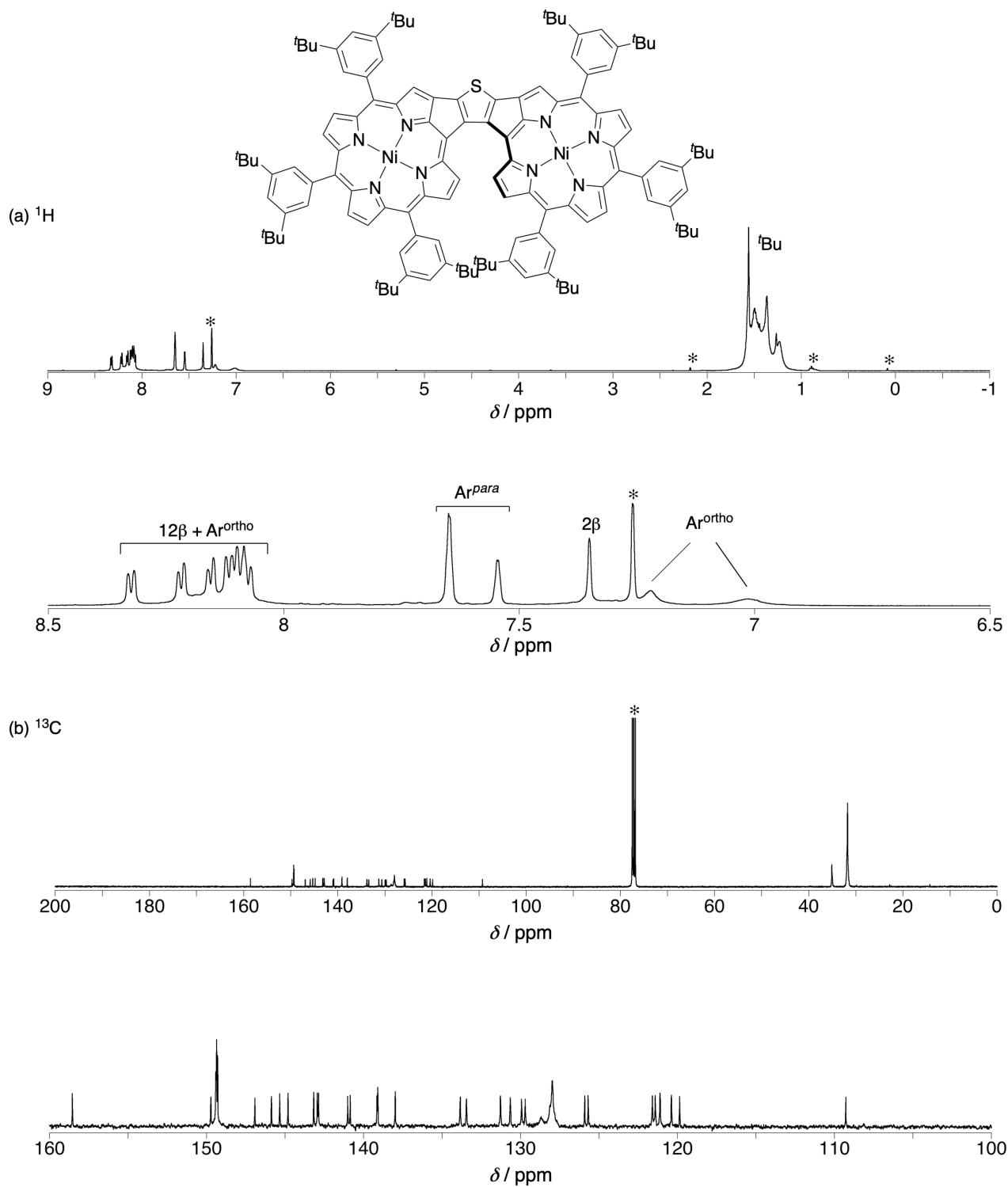


Figure S3. (a) ^1H and (b) ^{13}C NMR spectra of **1a** at 25 °C in CDCl_3 . Peaks marked with * arise from residual solvents.

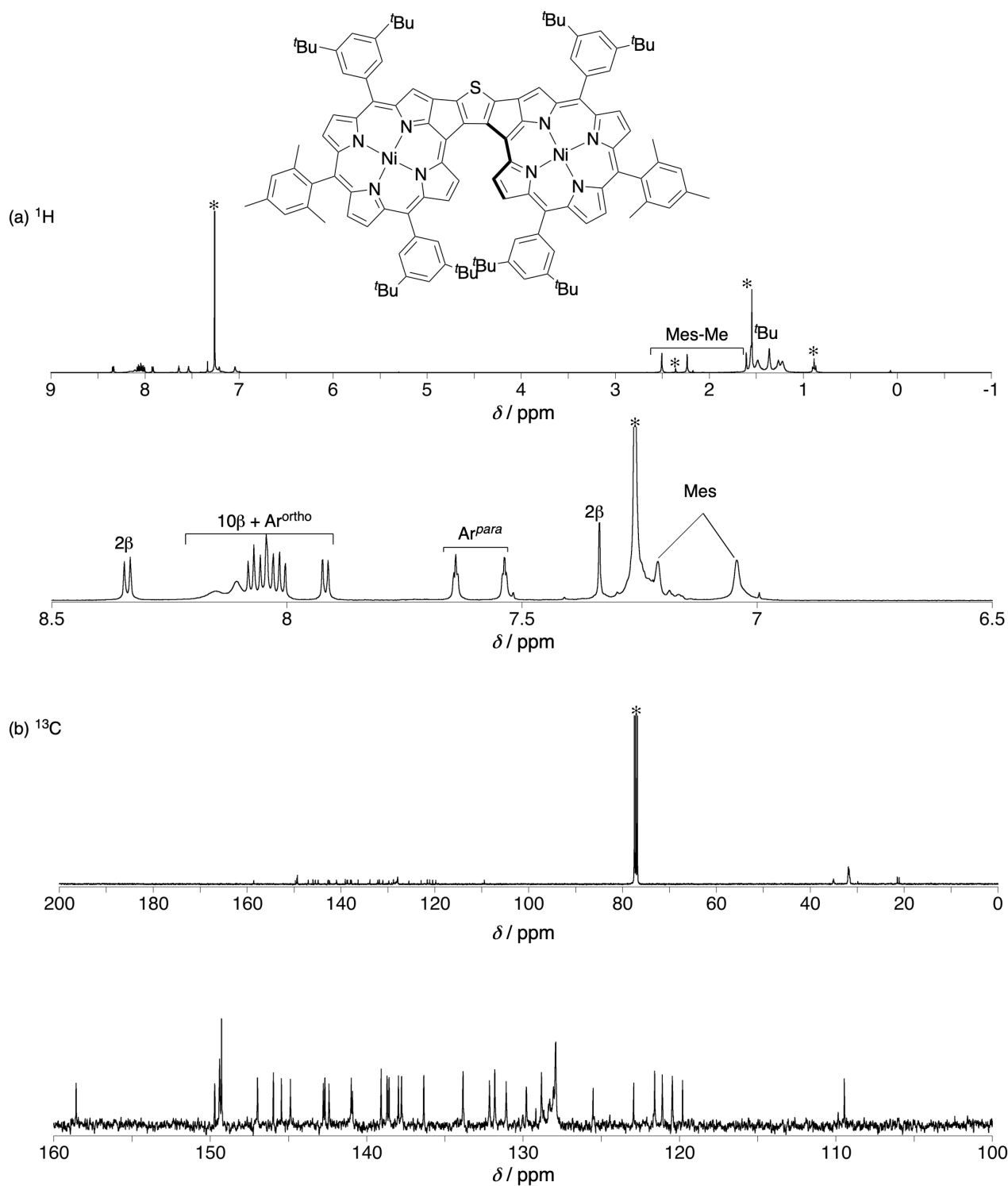


Figure S4. (a) ^1H and (b) ^{13}C NMR spectra of **1b** at 25 °C in CDCl_3 . Peaks marked with * arise from residual solvents.

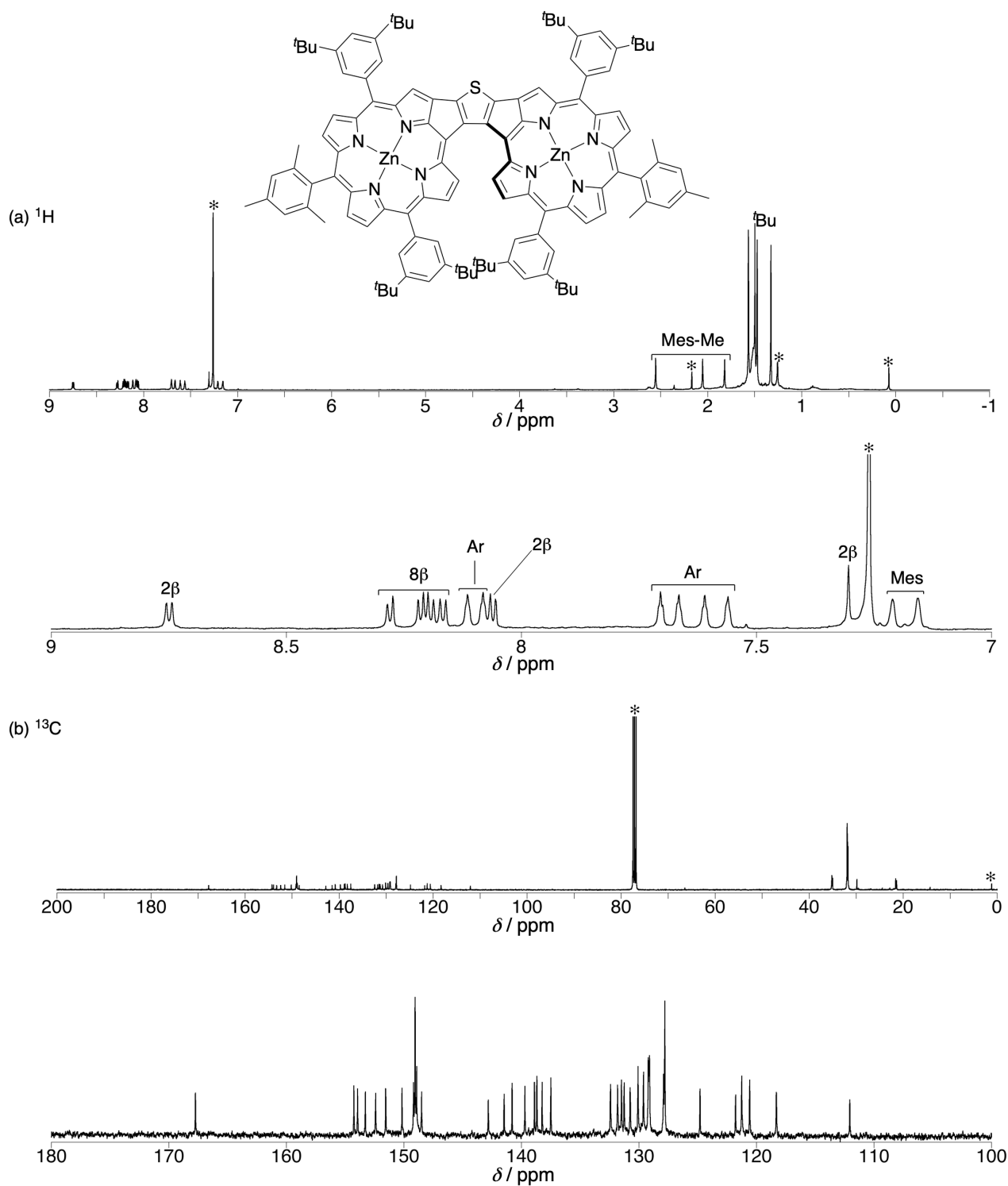
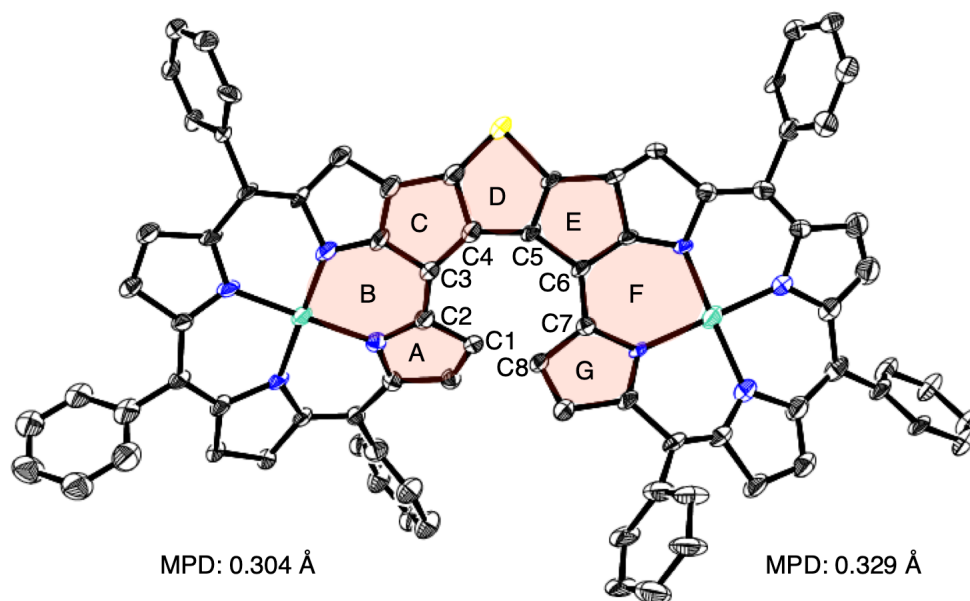


Figure S5. (a) ^1H and (b) ^{13}C NMR spectra of **2** at 25 °C in CDCl_3 . Peaks marked with * arise from residual solvents.

5. X-Ray Crystallographic Details

(a)



(b)

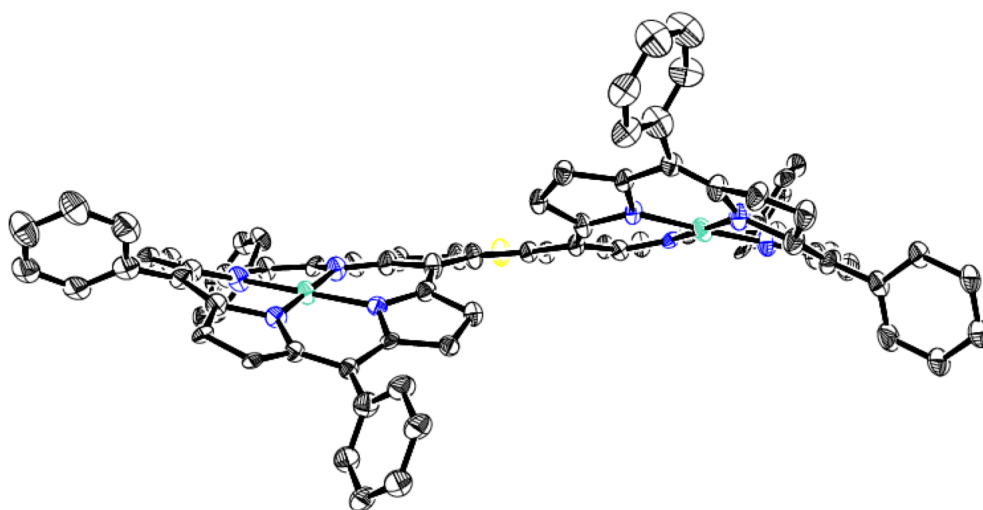


Figure S6. X-Ray crystal structure of the other independent molecule of **1a**: a) top view and b) side view. Thermal ellipsoids represent 50% probability. Solvent molecules, all hydrogen atoms, and *tert*-butyl groups are omitted for clarity. The disordered solvents are removed by the use of utility SQUEEZE in the PLATON software package^{S8}. Selected torsion angle [°]: \angle C1-C2-C3-C4 4(5); \angle C2-C3-C4-C5 -25(6); \angle C3-C4-C5-C6 -15(6); \angle C4-C5-C6-C7 -19(5); \angle C5-C6-C7-C8 -6(4).

Table S1. Crystal data using SQUEEZE of **1a**.

	1a
formula	2(C ₁₂₈ H ₁₄₀ N ₈ Ni ₂ S ₁)·7(CHCl ₃)
<i>M</i> _r	4715.48
<i>T</i> [K]	153
crystal system	triclinic
space group	<i>P</i> 1 (No.1)
<i>a</i> [Å]	19.992(4)
<i>b</i> [Å]	20.190(5)
<i>c</i> [Å]	21.414(3)
α [°]	69.720(15)
β [°]	63.048(12)
γ [°]	80.939(17)
<i>V</i> [Å ³]	7202(3)
<i>Z</i>	1
ρ_{calcd} [g·cm ⁻³]	1.087
<i>F</i> [000]	2478
crystal size [mm ³]	0.10×0.05×0.03
2 θ_{max} [°]	50.0
reflections collected	48710
independent reflections	35758
parameters	2611
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.1317
<i>wR</i> ₂ [all data]	0.3652
GOF	1.047
CCDC number	2093263

6. Racemic Inversion Barriers

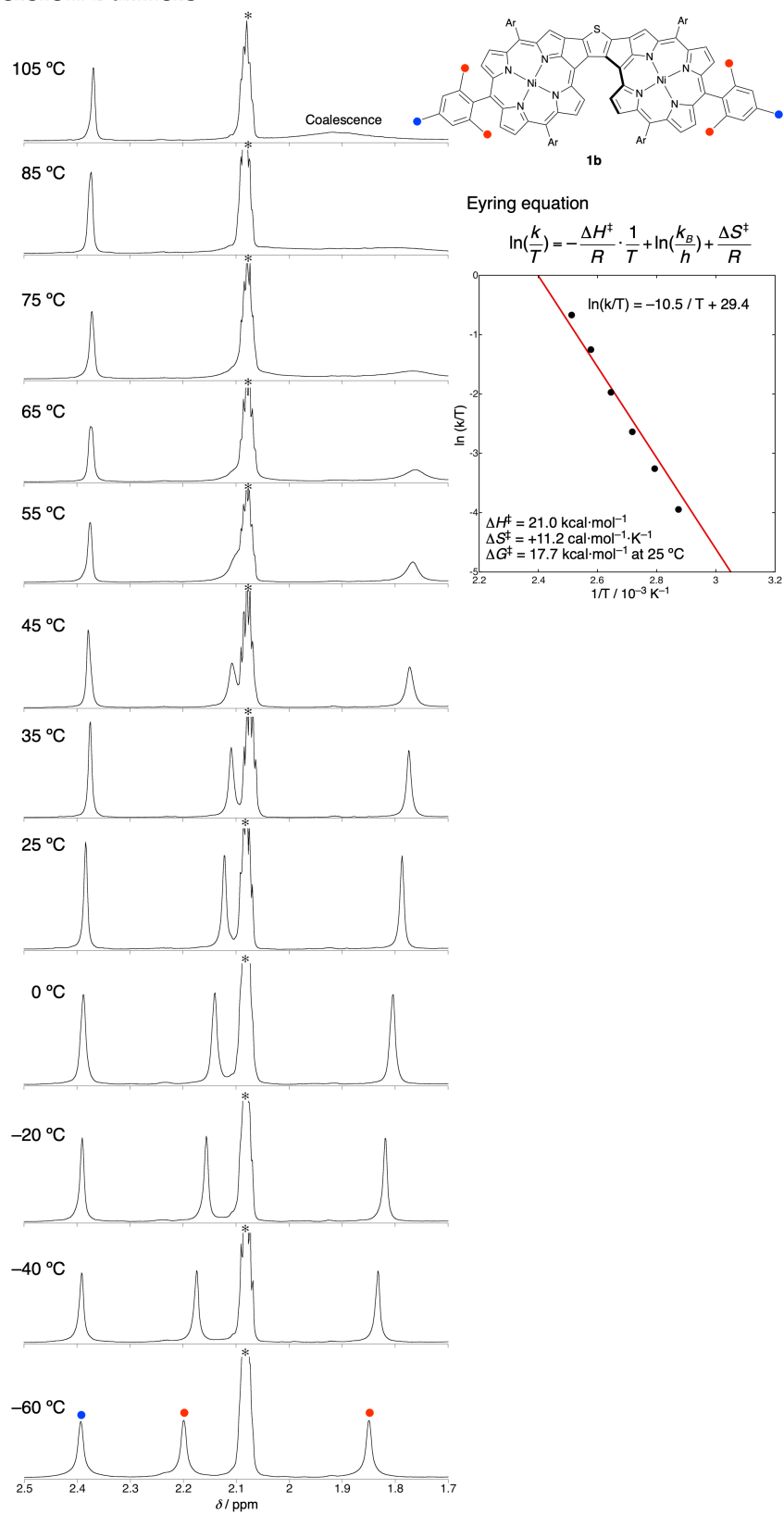


Figure S7. Temperature-dependent ^1H NMR spectra of **1b** in toluene- d_6 and Eyring plot for determination of inversion barrier. Peaks marked with * arise from residual solvents.

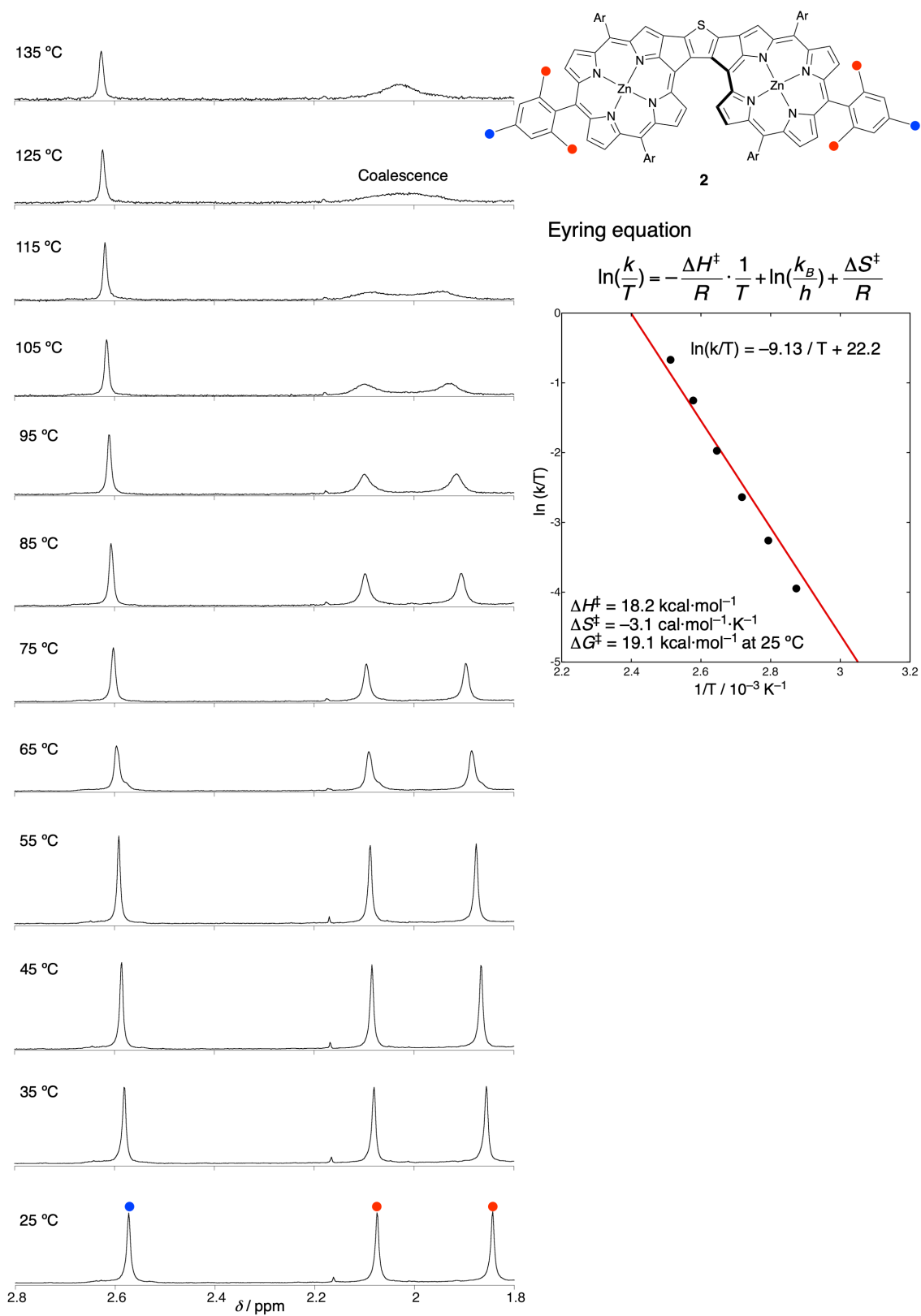


Figure S8. Temperature-dependent ^1H NMR spectra of **2** in $\text{C}_2\text{D}_2\text{Cl}_4$ and Eyring plot for determination of inversion barrier.

7. Optical Properties

Table S2. UV/Vis/NIR Absorption properties of porphyrin dimers **1** and **2** in CH₂Cl₂.

porphyrin	$\lambda_{\text{abs}} / \text{nm}$ ($\epsilon / 10^4 \text{M}^{-1}\cdot\text{cm}^{-1}$)
1a	426 (14), 462 (9.3), 557 (4.9), 615 (7.4), 864 (0.46), 975 (0.25)
1b	417 (11), 458 (9.1), 559 (4.9), 613 (7.8), 859 (0.47), 975 (0.23)
2	422 (11), 436 (11), 475 (11), 568 (4.5), 661 (7.1), 910 (0.40), 1040 (0.14)

8. Electrochemical Properties

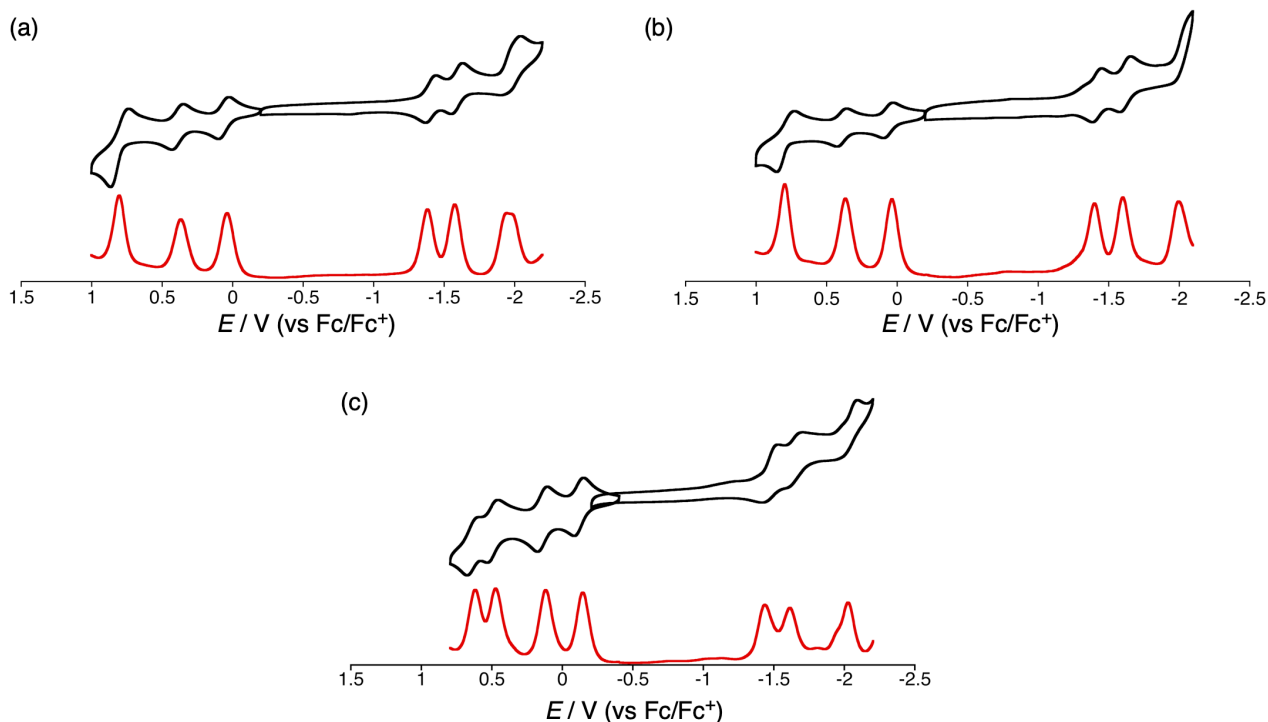


Figure S9. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of porphyrin dimers (a) **1a**, (b) **1b**, and (c) **2**. Redox potentials were determined by DPV. Solvent: CH₂Cl₂; scan rate: 0.05 V·s⁻¹; working electrode: glassy carbon; reference electrode: Ag/Ag⁺ (0.01 M AgNO₃); electrolyte: 0.1 M *n*-Bu₄NPF₆.

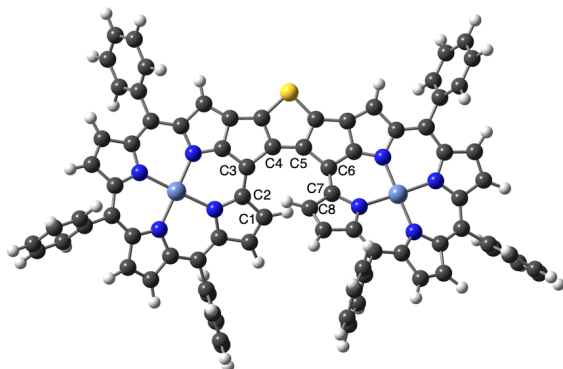
Table S3. Electrochemical oxidation and reduction potentials of thiophene-fused porphyrin dimers versus Fc/Fc⁺.

	E_{ox4}/V	E_{ox3}/V	E_{ox2}/V	E_{ox1}/V	E_{red1}/V	E_{red2}/V	E_{red3}/V	$E_{\text{g}}^{\text{CV}}/\text{V}$
1a	–	0.80	0.37	0.04	–1.38	–1.58	–1.94	1.42
1b	–	0.80	0.37	0.04	–1.40	–1.60	–2.00	1.44
2	0.62	0.47	0.12	–0.14	–1.44	–1.61	–2.03	1.30

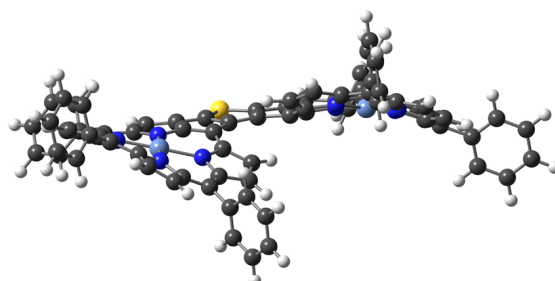
9. DFT Calculations

(a)

top view

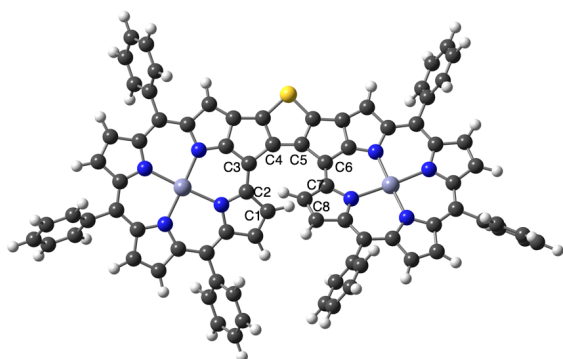


side view



(b)

top view



side view

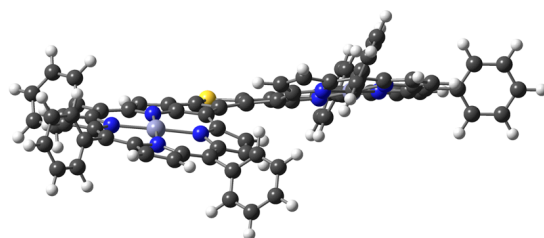


Figure S10. Optimized structures of (a) **1** and (b) **2**. Substituents at *meso*-positions were replaced with phenyl groups for clarity.

Table S4. Selected bond lengths and torsion angles of **1** and **2**.

	1	2
C1–C2 / Å	1.440	1.445
C2–C3 / Å	1.387	1.398
C3–C4 / Å	1.492	1.499
C4–C5 / Å	1.412	1.416
C5–C6 / Å	1.492	1.499
C6–C7 / Å	1.387	1.398
C7–C8 / Å	1.440	1.445
<hr/>		
∠ C1–C2–C3–C4 / °	0.9	2.4
∠ C2–C3–C4–C5 / °	26.2	21.8
∠ C3–C4–C5–C6 / °	5.3	8.6
∠ C4–C5–C6–C7 / °	26.2	21.8
∠ C5–C6–C7–C8 / °	0.9	2.4
<hr/>		
Sum of torsion angles / °	59.5	57.0

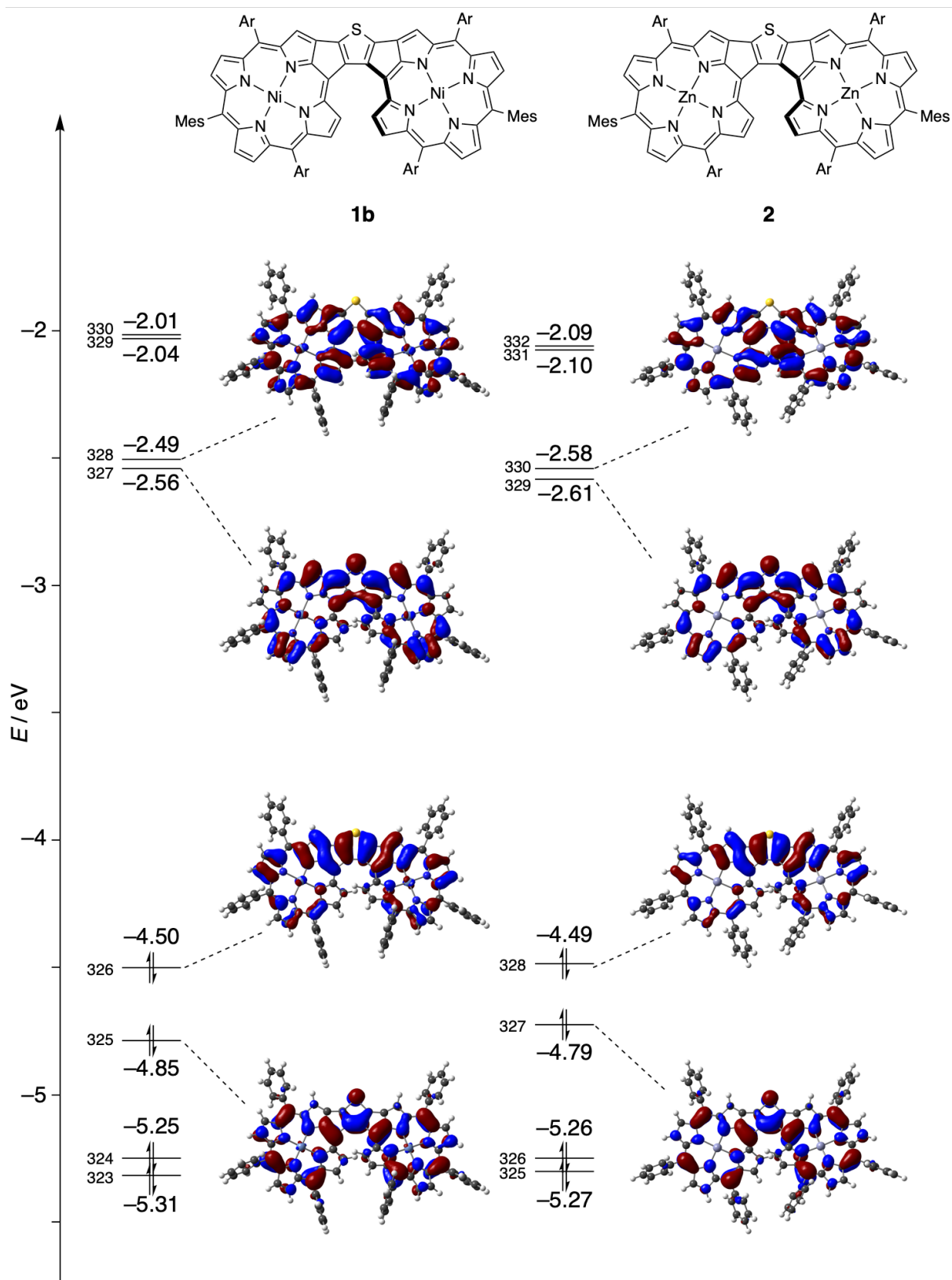


Figure S11. Selected Kohn-Sham orbitals of **1b** and **2**. Substituents at *meso*-positions were replaced with phenyl groups for clarity.

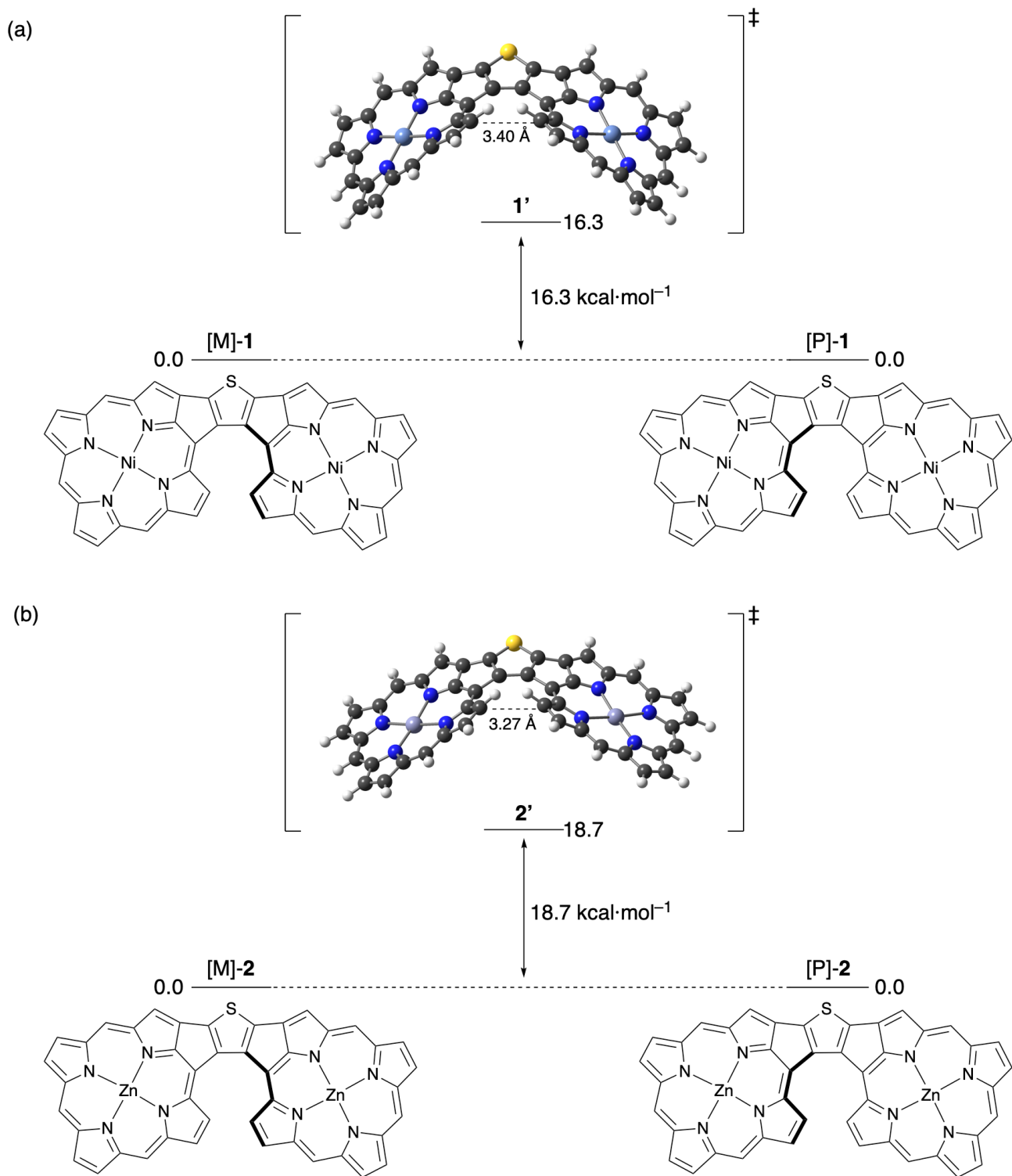


Figure S12. Racemization inversion processes of (a) **1'** and (b) **2'** with the relative Gibbs free energy (kcal·mol⁻¹) by DFT calculations with B3LYP/6-31G(d,p). The *meso*-aryl substituents and mesityl groups were replaced with hydrogen atoms to simplify the calculations.

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