Supporting Information for:

Switchable regioselectivity in PIFA-BF$_3$Et$_2$O mediated oxidative coupling of meso-brominated Ni(II) porphyrin

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1. Instrumentations and Materials

All NMR solvents were used as received. Chemical shifts of NMR spectra were reported in ppm down field from internal Me₄Si. Crystal data were collected with a Agilent Technologies SuperNova single-crystal diffractometer using a confocal monochromator with Mo Kα radiation (0.71073 Å) at 273 K. All UV-vis absorption spectra were recorded using a UV-3600 UV-Vis-NIR spectrophotometer (Shimadzu, Japan). High-resolution mass spectra (HRMS) were recorded on a VG ZAB-HS mass spectrometer under electron spray ionization (ESI) and a Bruker ultra fleXtreme MALDI-TOF/TOF spectrometer. All of the solvents were purified and distilled according to the standard procedure. The commercially obtained materials were used directly without further purification unless otherwise noted. PIFA (98%) and BF₃·Et₂O (98%) were purchased from Aldrich.

2. Optimization of the oxidative coupling

Table 1 Condition Screening of Oxidative Coupling of 1 with PIFA-BF₃·Et₂O

<table>
<thead>
<tr>
<th>entry</th>
<th>1/BF₃·Et₂O/PIFA (equiv)</th>
<th>yieldb (%)</th>
<th>time</th>
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<tr>
<td>1</td>
<td>1:0:0.5</td>
<td>0 0 90</td>
<td>1 h</td>
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<tr>
<td>2c</td>
<td>1:1:0</td>
<td>0 0 0</td>
<td>2 h</td>
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<tr>
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<td>0 75 0</td>
<td>30 min</td>
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<tr>
<td>6</td>
<td>1:1:1.5</td>
<td>0 68 0</td>
<td>30 min</td>
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<tr>
<td>7</td>
<td>1:0.5:0.5</td>
<td>80 trace 0</td>
<td>30 min</td>
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<tr>
<td>8</td>
<td>1:0.2:0.5</td>
<td>80 trace 0</td>
<td>1.5 h</td>
</tr>
<tr>
<td>9</td>
<td>1:0.5:1.0</td>
<td>0 75 0</td>
<td>30 min</td>
</tr>
</tbody>
</table>

aTo the stirred mixture of 1 and BF₃·Et₂O in CH₂Cl₂ was added dropwise a solution of PIFA in dry CH₂Cl₂ over 20 min under a nitrogen atmosphere. bIsolated yield. cCompound 1 was recovered.

Table S2. Reaction Conditions for Synthesizing Doubly and Triply Linked Porphyrin Dimers 5 and 6
To a stirred solution of 4 in dry CH₂Cl₂ was added PIFA and BF₃·Et₂O under a nitrogen atmosphere. "Isolated yield.

3. The absorption spectra of various linked Ni(II) porphyrin dimer

![Absorption Spectra](image)

**Fig. S1.** Ultraviolet-visible-infrared absorption spectra of fused porphyrin dimer 1 (red), 2 (blue), 3 (pink), 4 (green), 5 (yellow) and 6 (black) in CHCl₃.

4. The Procedure for the Synthesis of Singly Linked Porphyrin Dimers

For the *meso*-β linked 2

Under the nitrogen atmosphere, to a stirred solution of 1 (49 mg, 0.06 mmol) and BF₃·Et₂O (4 mg, 0.03 mmol, 0.5 equiv) in dry CH₂Cl₂ (50 mL) was added dropwise a solution of PIFA (13 mg, 0.03 mmol, 0.5 equiv) in dry CH₂Cl₂ (10 mL) over 20 min at RT. The reaction mixture was stirred for additional 10 min at the same temperature. Et₃N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with CHCl₃, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous
Na₂SO₄ and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). 2 (39 mg, 80%) was obtained after recrystallization from CHCl₃/CH₃OH.

1H NMR (400 MHz, CDCl₃, RT): δ = 9.66 (d, J = 5.0 Hz, 1H), 9.63 (s, 1H), 9.60 – 9.56 (m, 3H), 9.07 – 9.04 (m, 2H), 8.91 – 8.86 (m, 3H), 8.76 (d, J = 5.0 Hz, 2H), 8.66 (bs, 3H), 8.46 (d, J = 4.8 Hz, 1H), 8.10 (d, J = 1.7 Hz, 2H), 7.80 (d, J = 1.7 Hz, 2H), 7.71 – 7.68 (m, 4H), 1.48 – 1.40 (m, 7H).

1H NMR (400 MHz, CDCl₃, -40°C): δ = 9.66 (s, 1H), 9.68 (d, J = 5.0 Hz, 1H), 9.62 – 9.58 (m, 3H), 9.14 (d, J = 5.0 Hz, 1H), 9.10 (s, 1H), 8.96 (d, J = 5.0 Hz, 2H), 8.92 (d, J = 5.0 Hz, 1H), 8.80 (d, J = 5.0 Hz, 2H), 8.73– 8.67 (m, 3H), 8.47 (d, J = 4.8 Hz, 1H), 8.17 – 8.12 (m, 4H), 7.80 (d, J = 1.8 Hz, 2H), 7.71 (bs, 1H), 7.69 (s, 3H), 7.59 (s, 2H), 1.51 – 1.46 (m, 32H), 1.44 (s, 18H), 1.40 (s, 18H).

13C NMR (100 MHz, CDCl₃, RT): δ = 149.24, 149.09, 149.04, 145.90, 144.42, 143.90, 143.78, 143.62, 143.56, 143.34, 143.05, 142.43, 142.38, 142.24, 141.38, 139.55, 139.35, 137.88, 133.72, 133.68, 133.64, 133.20, 133.16, 133.12, 133.07, 132.52, 128.29, 128.90, 128.74, 121.46, 121.32, 121.11, 120.54, 112.16, 106.74, 102.76, 102.66, 102.47, 34.94, 31.67, 31.62.

HRMS (MALDI) m/z [M+H]+ calcd. for C₉₆H₁₀₀Br₂N₈Ni₂: 1642.5080, found 1642.5073; Ultraviolet-visible absorption : (in CHCl₃, λ max/nm, ε/mol⁻¹dm³cm⁻¹): 417 (2.14 × 10⁵), 431 (1.80 × 10⁵), 534 (3.57 × 10⁴).

For the meso-meso linked 4

Under the nitrogen atmosphere, to a stirred solution of 1 (49 mg, 0.06 mmol) in dry CH₂Cl₂ (50 mL) was added dropwise a solution of PIFA (13 mg, 0.03 mmol, 0.5 equiv) in dry CH₂Cl₂ (10 mL) over 20 min at RT. The reaction mixture was stirred for additional 50 min at the same temperature. Et₃N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with CHCl₃, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous Na₂SO₄ and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). 4 (44 mg, 90%) was obtained after recrystallization from CHCl₃/CH₃OH.

1H NMR (400 MHz, CDCl₃, RT): δ = 9.58 (d, J = 5.0 Hz, 4 H), 8.85 (d, J = 5.0 Hz, 4 H), 8.53(d, J = 5.0 Hz, 4 H), 8.02 (d, J = 5.0 Hz, 4 H), 7.83 (d, J = 1.6 Hz, 8 H), 7.66 (d, J = 4.8 Hz, 2H), 6.20 (d, J = 5.0 Hz, 2H), 1.54 (s, 36H), 1.51 (s, 36H).

13C NMR (100 MHz, CDCl₃, RT): δ = 149.00, 146.84, 143.95, 142.72, 142.26, 139.41, 133.54, 133.10, 133.00, 128.71, 121.62, 121.30, 115.83, 102.97, 34.94, 31.60..

HRMS (MALDI) m/z [M+H]+ calcd. for C₉₆H₁₀₀Br₂N₈Ni₂: 1643.5158, found 1643.5175; Ultraviolet-visible absorption : (in CHCl₃, λ max/nm, ε/mol⁻¹dm³cm⁻¹): 421 (1.64 × 10⁵), 449 (1.84 × 10⁵), 539 (4.20 × 10⁴).

5. The Procedure for the Synthesis of meso-β, meso-β Doubly Fused Dimer

Under the nitrogen atmosphere, to a stirred solution of 1 (49 mg, 0.06 mmol) and BF₃·Et₂O (4 mg, 0.03 mmol, 0.5 equiv) in dry CH₂Cl₂ (40 mL) was added dropwise a solution of PIFA (26 mg, 0.06 mmol, 1 equiv) in dry CH₂Cl₂ (10 mL) over 20 min at RT. The reaction mixture was stirred for additional 10 min at the same temperature. Et₃N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with CHCl₃, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous Na₂SO₄ and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). 3 (37 mg, 75%) was obtained after recrystallization from CHCl₃/CH₃OH.
$^1$H NMR (400 MHz, CDCl$_3$, RT): $\delta$ = 9.21 (d, $J$ = 5.0 Hz, 2H), 9.16 (d, $J$ = 4.9 Hz, 2H), 8.78 (s, 2H), 8.55 – 8.51 (m, 2H), 8.48 (d, $J$ = 5.0 Hz, 4H), 7.76 (bs, 2H), 7.64 (bs, 2H), 7.46 (d, $J$ = 5.1 Hz, 2H), 1.70 – 1.20 (m, 72H).

$^1$C NMR (100 MHz, CDCl$_3$, RT): $\delta$ = 149.39, 145.98, 144.82, 143.85, 142.98, 142.51, 142.13, 141.88, 139.67, 139.64, 138.68, 137.77, 137.69, 137.49, 133.53, 133.44, 133.40, 133.26, 132.36, 128.68, 128.46, 126.49, 124.04, 121.55, 121.42, 120.40, 113.23, 103.98, 34.81, 31.59.

HRMS (ESI) m/z [M]$^+$ calcd. for C$_{96}$H$_{98}$Br$_2$N$_8$Ni$_2$: 1640.4924, found 1640.4950; Ultraviolet-visible-infrared absorption: (in CHCl$_3$, $\lambda_{\text{max}}$/nm, $\varepsilon$/mol$^{-1}$dm$^3$cm$^{-1}$): 412 (0.63 $\times$ 10$^5$), 487 (0.96 $\times$ 10$^5$), 526 (0.72 $\times$ 10$^5$), 738 (4.07 $\times$ 10$^4$).

6. The Procedure for the Synthesis of meso-meso, $\beta$-$\beta$ Doubly Fused Dimer

Under the nitrogen atmosphere, a solution of 1 (49 mg, 0.06 mmol) and PIFA (26 mg, 0.06 mmol, 1 equiv) in dry CH$_2$Cl$_2$ (50 mL) was stirred at RT for 1 h. When the porphyrin monomer was completely consumed, BF$_3$·Et$_2$O (4 mg, 0.03 mmol, 0.5 equiv) was added to the mixture. The mixture was stirred for additional 10 min at the same temperature. Et$_3$N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with CHCl$_3$, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous Na$_2$SO$_4$ and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). 5 (41 mg, 84%) was obtained after recrystallization from CHCl$_3$/CH$_3$OH.

$^1$H NMR (400 MHz, CDCl$_3$, -40°C): $\delta$ = 8.84 (d, $J$ = 4.9 Hz, 2H), 8.61 (d, $J$ = 4.9 Hz, 2H), 8.59 (d, $J$ = 5.0 Hz, 2H), 8.57 (d, $J$ = 5.0 Hz, 2H), 7.74 (bs, 2H), 7.63 (bs, 2H), 7.48 (d, $J$ = 5.1 Hz, 2H), 7.15 (s, 2H), 6.98 (s, 2H), 1.67 (s, 18H), 1.64 (s, 18H), 1.43 (s, 18H), 1.22 (s, 18H).

HRMS (ESI) m/z [M]$^+$ calcd. for C$_{96}$H$_{98}$Br$_2$N$_8$Ni$_2$: 1640.4924, found 1640.4950; Ultraviolet-visible-infrared absorption: (in CHCl$_3$, $\lambda_{\text{max}}$/nm, $\varepsilon$/mol$^{-1}$dm$^3$cm$^{-1}$): 412 (0.63 $\times$ 10$^5$), 487 (0.96 $\times$ 10$^5$), 526 (0.72 $\times$ 10$^5$), 738 (4.07 $\times$ 10$^4$).

7. The Procedure for the Synthesis of $\beta$-$\beta$, meso-meso, $\beta$-$\beta$ Triply Fused Dimer

Under the nitrogen atmosphere, a solution of 1 (49 mg, 0.06 mmol) and PIFA (26 mg, 0.06 mmol, 1 equiv) in dry CH$_2$Cl$_2$ (50 mL) was stirred at RT for 1 h. When the porphyrin monomer was completely consumed, BF$_3$·Et$_2$O (4 mg, 0.03 mmol, 0.5 equiv) was added to the mixture. The mixture was stirred for additional 10 min at the same temperature. Et$_3$N (0.2 mL) was added to the reaction mixture. The reaction mixture was poured into water and extracted with CHCl$_3$, then washed with saturated sodium bicarbonate aqueous solution twice. The combined extract was dried over anhydrous Na$_2$SO$_4$ and then evaporated to dryness. The crude residue was purified by column chromatography (silica-gel). 6 (39 mg, 80%) was obtained after recrystallization from CHCl$_3$/petroleum ether.

$^1$H NMR (400 MHz, VCDCl$_3$/VCS$_2$ = 4:1, RT): $\delta$ = 8.52 (d, $J$ = 4.9 Hz, 4H), 7.77 (d, $J$ = 4.9 Hz, 4H), 7.60 (s, 4H), 7.54 (d, $J$ = 8.5 Hz, 8H), 7.47 (s, 4H), 7.15 (s, 2H), 1.43 (s, 72H).

$^{13}$C NMR (100 MHz, VCDCl$_3$/VCS$_2$ = 4:1, RT): $\delta$ = 149.15, 147.45, 146.53, 145.52, 145.47, 138.37, 134.76, 132.04, 131.70, 127.65, 127.49, 125.01, 121.40, 113.31, 107.89, 34.81, 31.59.
HRMS (ESI) m/z [M]+ calcd. for C₉₆H₉₀Br₂N₂Ni₂: 1638.4767, found 1638.4787; Ultraviolet-visible-infrared absorption: (in CHCl₃, λ_max/nm, ε/mmol⁻¹dm³cm⁻¹): 411 (1.58 × 10⁵), 572 (1.23 × 10⁴), 651 (1.13 × 10⁴), 864 (1.72 × 10⁴), 937 (2.10 × 10⁴).

8. **S_NAr reaction of 2**

2 (40 mg, 0.02 mmol), Cs₂CO₃ (33 mg, 0.10 mmol, 5 equiv) and phenol (9 mg, 0.10 mmol, 5 equiv) were added to a 25 mL two-necked round bottom flask, then the flask was evacuated and backfilled with N₂ for 3 times. DMF (5 mL) was added using a syringe, then the reaction was heated to 100°C. The solution was continuously stirred at the temperature for 1.5 h. When compound 2 was completely consumed, the mixture was cooled down to room temperature, and water (5.0 mL) was added to precipitate the product. 8 (33 mg, 81%) was obtained after recrystallization from CHCl₃/CH₃OH.

1H NMR (400 MHz, CDCl₃, RT): δ = 9.69 (s, 1H), 9.36 (d, J = 4.9 Hz, 1H), 9.31 – 9.27 (m, 3H), 9.10 (s, 1H), 9.02 (d, J = 4.9 Hz, 1H), 8.88 – 8.78 (m, 3H), 8.48 (d, J = 4.8 Hz, 1H), 8.16 – 8.08 (m, 4H), 7.83 (d, J = 1.7 Hz, 2H), 7.72 – 7.60 (m, 4H), 7.24 – 7.19 (m, 2H), 6.95 (t, J = 7.5 Hz, 2H), 1.48 – 1.40 (m, 72H).

13C NMR (100 MHz, CDCl₃, RT): δ = 164.39, 164.33, 164.18, 164.14, 149.21, 149.06, 149.01, 146.27, 144.70, 143.88, 143.62, 143.40, 143.33, 143.31, 143.05, 143.02, 141.44, 139.85, 139.65, 139.63, 139.40, 139.37, 139.13, 137.95, 133.09, 132.97, 132.79, 132.69, 132.10, 132.00, 129.62, 129.30, 128.90, 128.76, 128.30, 128.13, 128.09, 121.80, 121.77, 121.36, 121.22, 120.99, 120.91, 120.35, 116.49, 111.63, 106.23, 35.01, 34.97, 31.69, 31.64.

HRMS (MALDI) m/z [M]+ calcd. for C₁₀₈H₁₁₀O₂N₈Ni₂: 1667.7486, found 1667.7500; Ultraviolet-visible absorption: (in CHCl₃, λ_max/nm, ε/mmol⁻¹dm³cm⁻¹): 419 (2.19 × 10⁵), 432 (2.03 × 10⁵), 530 (4.20 × 10⁴).

9. **Demetallation of 2, 3 and 6**

For meso-β singly linked dimer 7 Porphyrin dimer 2 (82 mg, 0.05 mmol) was dissolved in dry CH₂Cl₂ (20 mL) in a 100 mL round-bottomed flask. The solution was cooled to -10 °C, and then treated with 0.5 mL of H₂SO₄/TFA (1:10) 30 min. After neutralization by aqueous NaHCO₃, the solution was extracted with CH₂Cl₂, washed by brine, dried over anhydrous Na₂SO₄, and the solvent was removed undervacuum. The crude residue was purified by column chromatography (silica-gel). 7 (43 mg, 57%) was obtained after recrystallization from CHCl₃/CH₃OH.

1H NMR (400 MHz, CDCl₃, RT): δ = 9.89 (d, J = 4.9 Hz, 1H), 9.81 – 9.74 (m, 4 H), 9.70 (s, 1H), 9.24 (d, J = 4.9 Hz, 1H), 9.00 (d, J = 4.6 Hz, 2H), 8.97 (d, J = 4.8 Hz, 1H), 8.91 (d, J = 4.6 Hz, 2H), 8.81 (d, J = 4.7 Hz, 1H), 8.75 (d, J = 4.7 Hz, 2H), 8.65 (d, J = 4.7 Hz, 1H), 8.37 (d, J = 1.8 Hz, 2H), 8.14 (d, J = 1.4 Hz, 2H), 8.06 – 7.99 (4 H, m), 7.79 – 7.72 (4 m, 4 H), 1.51 – 1.49 (m, 36H), 1.49 – 1.47 (m, 36H), -2.30 (s, 2 H), -2.55 (s, 2 H).

13C NMR (100 MHz, CDCl₃, RT): δ = 149.41, 149.39, 149.27, 149.25, 149.20, 149.02, 148.91, 148.87, 146.27, 144.33, 140.72, 140.43, 140.27, 138.73, 138.64, 133.91, 133.81, 132.41, 132.32, 132.09, 131.93, 131.67, 131.30, 131.02, 130.52, 130.47, 130.40, 129.97, 129.95, 129.85, 122.65, 122.43, 121.97, 121.44, 121.26, 113.64, 107.28, 103.66, 103.46, 35.03, 35.03, 31.72, 31.69.

HRMS (MALDI) m/z [M+H]+ calcd. for C₁₀₈H₁₀₄O₂N₂Br₂: 1667.7486, found 1667.7500; Ultraviolet-visible absorption: (in CHCl₃, λ_max/nm, ε/mmol⁻¹dm³cm⁻¹): 419 (2.19 × 10⁵), 432 (2.03 × 10⁵), 530 (4.20 × 10⁴).
For fused dimers H<sub>r</sub>-3 and H<sub>r</sub>-6

![Diagram of porphyrin dimers](image)

Scheme S1. Demetalation reaction of 3 and 6

Porphyridimer 3 (50 mg, 0.03 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) in a 50 mL round-bottomed flask. The solution was treated with concentrated H<sub>2</sub>SO<sub>4</sub> (0.1 mL) 30 min at RT. After neutralization by aqueous NaHCO<sub>3</sub>, the solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed undervacuum. The crude residue was purified by column chromatography (silica-gel). H<sub>r</sub>-3 (35 mg, 76%) was obtained after recrystallization from CHCl<sub>3</sub>/CH<sub>3</sub>OH.

**H<sub>r</sub>-3:**

1H NMR (400 MHz, CDCl<sub>3</sub>, RT): δ = 9.47 (d, J = 4.6 Hz, 2H), 9.26 – 9.20 (m, 4H), 9.10 (s, 2H), 8.62 – 8.56 (m, 4H), 8.49 (d, J = 4.8 Hz, 2H), 8.11 (d, J = 1.4 Hz, 4H), 7.98 (d, J = 1.4 Hz, 4H), 7.85 – 7.78 (m, 2H), 1.59 – 1.56 (m, 72H), 0.52 (s, 4H).

13C NMR (100 MHz, CDCl<sub>3</sub>, RT): δ = 149.33, 149.25, 147.07, 146.93, 146.10, 145.79, 145.26, 145.12, 144.51, 143.41, 143.23, 142.54, 142.31, 140.24, 138.37, 137.65, 135.61, 135.50, 135.19, 129.98, 129.88, 124.96, 124.19, 121.62, 121.41, 105.43, 94.92, 35.17, 35.11, 31.83, 31.74.

HRMS (MALDI) m/z [M+H]<sup>+</sup> calcd. for C<sub>96</sub>H<sub>102</sub>Br<sub>2</sub>N<sub>8</sub>: 1527.6651, found 1527.6655; Ultraviolet-visible-infrared absorption : (in CHCl<sub>3</sub>, λ<sub>max</sub>/nm, ε/mol·dm<sup>3</sup>·cm<sup>-1</sup>): 425 (1.31 × 10<sup>5</sup>), 501 (6.70 × 10<sup>4</sup>), 545 (5.45 × 10<sup>4</sup>), 616 (4.35 × 10<sup>4</sup>), 821 (5.50 × 10<sup>4</sup>).

**H<sub>r</sub>-6:** Following the same procedure for demetalation of 3.

1H NMR (400 MHz, V<sub>CDCl<sub>3</sub>/VCS<sub>2</sub> = 4:1, RT): δ = 8.46 – 8.38 (m, 6H), 7.65 – 7.63 (m, 6H), 7.61 – 7.57 (m, 12H), 1.46 – 1.42 (m, 72H).

13C NMR (100 MHz, V<sub>CDCl<sub>3</sub>/VCS<sub>2</sub> = 4:1, RT): δ = 148.94, 147.60, 146.65, 145.47, 145.45, 138.83, 133.97, 128.95, 128.18, 125.84, 125.81, 125.53, 121.33, 114.28, 107.83, 34.73, 31.57.

HRMS (MALDI) m/z [M+H]<sup>+</sup> calcd. for C<sub>96</sub>H<sub>100</sub>Br<sub>2</sub>N<sub>8</sub>: 1525.6494, found 1525.6508; Ultraviolet-visible-infrared absorption : (in CHCl<sub>3</sub>, λ<sub>max</sub>/nm, ε/mol·dm<sup>3</sup>·cm<sup>-1</sup>): 415 (1.19 × 10<sup>5</sup>), 482 (5.90 × 10<sup>4</sup>), 565 (1.24 × 10<sup>5</sup>), 1044 (2.73 × 10<sup>4</sup>), 1090 (3.07 × 10<sup>4</sup>).
10. NMR Spectra of Directly Linked Porphyrin Dimers

Figure S2. $^1$H NMR spectrum of 2 (400 MHz, CDCl$_3$ at 25°C).

Figure S3. $^1$H NMR spectrum of 2 (400 MHz, CDCl$_3$ at -40°C).
Figure S4. $^{13}$C NMR spectrum of 2 (100 MHz, CDCl$_3$ at 25°C).

Figure S5. $^1$H NMR spectrum of 3 (400 MHz, CDCl$_3$ at 25°C).
Figure S6. $^{13}$C NMR spectrum of 3 (100 MHz, CDCl$_3$ at 25°C).

Figure S7. $^1$H NMR spectrum of 4 (400 MHz, CDCl$_3$ at 25°C).
Figure S8. $^{13}$C NMR spectrum of 4 (100 MHz, CDCl$_3$ at 25°C).

Figure S9. $^1$H NMR spectrum of 5 (400 MHz, CDCl$_3$ at 25°C).
Figure S10. $^1$H NMR spectrum of 5 (400 MHz, CDCl$_3$ at -40°C).

Figure S11. $^{13}$C NMR spectrum of 5 (100 MHz, CDCl$_3$ at 25°C).
Figure S12. $^1$H NMR spectrum of 6 (400 MHz, V$_{CDCl_3}$/V$_{CS_2}$ = 4:1 at 25°C).

Figure S13. $^{13}$C NMR spectrum of 6 (100 MHz, V$_{CDCl_3}$/V$_{CS_2}$ = 4:1 at 25°C, $\delta$ ($^{13}$CS$_2$) = 192.51).
Figure S14. $^1$H NMR spectrum of 7 (400 MHz, CDCl$_3$ at 25°C).

Figure S15. $^{13}$C NMR spectrum of 7 (100 MHz, CDCl$_3$ at 25°C).
Figure S16. $^1$H NMR spectrum of 8 (400 MHz, CDCl$_3$ at 25°C).

Figure S17. $^{13}$C NMR spectrum of 8 (100 MHz, CDCl$_3$ at 25°C).
Figure S18. $^1$H NMR spectrum of H4-3 (400 MHz, CDCl$_3$ at 25°C).

Figure S19. $^{13}$C NMR spectrum of H4-3 (100 MHz, CDCl$_3$ at 25°C).
Figure S20. $^1$H NMR spectrum of H4-6 (400 MHz, $\text{CDCl}_3/\text{CS}_2 = 4:1$ at 25°C).

Figure S21. $^{13}$C NMR spectrum of H4-6 (100 MHz, $\text{CDCl}_3/\text{CS}_2 = 4:1$ at 25°C, $\delta$ ($^{13}$CS) = 192.45).
11. Crystal Data for 2

<table>
<thead>
<tr>
<th>Compound reference</th>
<th>2</th>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{96}H_{100}Br_{2}N_{8}Ni_{2}</td>
</tr>
<tr>
<td>Formula Mass</td>
<td>1643.02</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>38.7(10)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>9.0001(13)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>33.3200(3)</td>
</tr>
<tr>
<td>(\alpha/°)</td>
<td>90.00</td>
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<tr>
<td>(\beta/°)</td>
<td>109.69</td>
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<tr>
<td>(\gamma/°)</td>
<td>90.00</td>
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<tr>
<td>Unit cell volume/(\text{Å}^3)</td>
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<tr>
<td>Temperature/K</td>
<td>273(2)</td>
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<tr>
<td>Space group</td>
<td>(P21/c)</td>
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<tr>
<td>No. of formula units per unit cell, (Z)</td>
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<tr>
<td>No. of reflections measured</td>
<td>47293</td>
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<tr>
<td>No. of independent reflections</td>
<td>19023</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.0420</td>
</tr>
<tr>
<td>Final (R_I) values ((I &gt; 2\sigma(I)))</td>
<td>0.0994</td>
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<tr>
<td>Final (wR(F^2)) values ((I &gt; 2\sigma(I)))</td>
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<tr>
<td>Final (R_I) values (all data)</td>
<td>0.1410</td>
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<tr>
<td>Final (wR(F^2)) values (all data)</td>
<td>0.3090</td>
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