Supplementary Information for

Regioselective phenylene-fusion reactions of Ni(II)-porphyrins controlled by an electron-withdrawing meso-substituent


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Contents

1. Possible Isomers as Doubly Phenylene-Fused Porphyrins
2. Instrumentation and Materials
3. Experimental Procedures and Compound Data
4. X-Ray Crystal Structures
5. DFT Calculations
6. Femtosecond Transient Absorption Measurements
7. TPA Spectra and Z-Scan Curves
8. NICS Calculations and ACID Plot
9. Electrochemical Properties
10. References
1. Possible Isomers as Doubly Phenylene-Fused Porphyrins

Scheme S1. Seven different structures as doubly phenylene-fused porphyrins.
2. Instrumentation and Materials

H NMR (600 MHz) and 13C NMR (151 MHz) spectra were taken on a JEOL ECA-600 spectrometer. Chemical shifts are reported on a delta scale in ppm relative to residual CHCl, (δ = 7.26 ppm) or 2,3,5,6-tetradeuteriopyridine (δ = 7.58 ppm) for 1H NMR, and to CDCl, (δ = 77.16 ppm) for 13C NMR. Spectroscopic grade solvents were used for all spectroscopic studies without further purification. UV/Vis/NIR absorption spectra were recorded on a Shimadzu UV-3600PC spectrometer. Atmospheric pressure chemical ionization time-of-flight mass (APCI-TOF-MS) spectra were recorded on a Bruker micrTOF instrument. Preparative separations were performed by silica gel chromatography (Wako gel C-200, C-300, or C-400) and gel permeation chromatography (Bio-Rad Bio-Beads S-X1, packed with toluene). CH2Cl2, MeNO2, and toluene were distilled from CaH2. THF was purified by passing through a neutral alumina column under N2. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.
3. Experimental Procedures and Compound Data

**Synthesis of 2e and 3**: A flask containing 1e (17.6 mg, 18 µmol) was purged with argon, and then charged with CHCl₃ (1.5 mL). A solution of FeCl₃ (28.4 mg, 180 µmol) and DDQ (40.0 mg, 180 µmol) in MeNO₂ (0.5 mL) was added slowly to the mixture. The mixture was stirred at room temperature for 5 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ solution. The organic phase was separated and washed with water and brine, and dried over anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography eluting with CHCl₃/hexane. Recrystallization from CHCl₃/methanol gave 2e (5.0 mg, 5.1 µmol, 29%) and 3 (3.2 mg, 3.3 µmol, 18%)

2e: H NMR (600 MHz, CDCl₃, 25 °C): δ = 8.91 (d, J = 5.0 Hz, 2H, β), 8.64 (d, J = 5.0 Hz, 2H, β), 7.91 (d, J = 1.4 Hz, 2H, Ar), 7.74 (d, J = 1.8 Hz, 2H, Ar), 7.70 (s, 2H, β), 7.69 (t, J = 1.8 Hz, 1H, Ar), 7.10 (d, J = 1.4 Hz, 2H, Ar), 1.53 (s, 18H, tert-butyl), 1.50 (s, 18H, tert-butyl), and 1.47 (s, 18H, tert-butyl) ppm; ¹³C NMR (151 MHz, CDCl₃, 25 °C): δ = 155.78, 152.35, 149.96, 148.08, 147.56, 147.12, 145.76, 141.64, 141.36, 136.54, 133.21, 130.75, 130.34, 130.13, 129.38, 128.95, 127.59, 124.19, 121.98, 121.03, 118.68, 35.42, 35.24, 35.14, 31.79, 31.31, and 29.18 ppm; APCI-TOF-MS: m/z = 971.4658. Calcd for C₆₂H₆₇O₂N₅5Ni: 971.4654 [M] – 1

UV/Vis (CHCl₃): λmax (ε [M cm⁻¹]) = 441 (7.81 × 10⁴), 521 (4.18 × 10⁴), 624 (5.79 × 10³), 732 (3.42 × 10³), and 814 nm (1.91 × 10³).

3: H NMR (600 MHz, CDCl₃, 25 °C): δ = 9.10 (d, J = 5.0 Hz, 1H, β), 8.78 (d, J = 5.0 Hz, 1H, β), 8.76 (d, J = 5.0 Hz, 1H, β), 8.64 (d, J = 5.0 Hz, 2H, Ar), 8.58 (d, J = 5.0 Hz, 1H, β), 8.48 (d, J = 5.0 Hz, 1H, β), 7.95-7.93 (m, 2H, Ar + β), 7.79 (d, J = 1.9 Hz, 2H, Ar), 7.76 (d, J = 1.9 Hz, 2H, Ar), 7.75-7.72 (m, 2H, Ar), 7.04 (s, 1H, Ar), 1.54 (s, 9H, tert-butyl), 1.50 (s, 18H, tert-butyl), and 1.46 (s, 9H, tert-butyl) ppm; ¹³C NMR (151 MHz, CDCl₃, 25 °C): δ = 154.74, 153.07, 150.24, 149.72, 149.48, 149.98, 147.89, 147.69, 146.55, 146.23, 145.23, 140.90, 139.33, 138.11, 137.89, 137.54, 135.64, 134.43, 133.49 (overlap), 131.19, 129.35, 128.71, 128.61, 128.22, 127.43, 126.46, 125.99, 123.87, 122.57, 121.72 (overlap), 121.35, 116.54, 35.43, 35.23, 35.17 (overlap), 31.81, 31.21, 29.87, and 29.13 ppm; APCI-TOF-MS: m/z = 973.4828. Calcd for C₆₂H₆₉N₅NiO₂: 973.4810 [M]; UV/Vis (CHCl₃): λmax (ε [M cm⁻¹]) = 439 (6.64 × 10³), 473 (5.23 × 10³), 575 (5.65 × 10³), 622 (4.98 × 10³), and 669 nm (3.66 × 10³).
**Figure S 1.** $^1$H NMR spectrum of 2e in CDCl$_3$ at 25 °C. *Solvent and impurities.

**Figure S 2.** $^{13}$C NMR spectrum of 2e in CDCl$_3$ at 25 °C. *Solvent.

**Figure S 3.** Observed (top) and simulated (bottom) HR-APCI-TOF MS of 2e.
Figure S 4. UV/Vis absorption spectrum of 2e in CHCl₃.

Figure S 5. H NMR spectrum of 3 in CDCl₃ at 25 °C. *Solvent and impurities.

Figure S 6. ¹³C NMR spectrum of 3 in CDCl₃ at 25 °C. *Solvent and impurity.
Figure S 7. Observed (top) and simulated (bottom) HR-APCI-TOF MS of 3.

Figure S 8. UV/Vis absorption spectrum of 3 in CH₂Cl₂.

**Synthesis of 2f:** A flask containing 1f (20.0 mg, 18 μmol) was purged with argon, and then charged with CH₂Cl₂ (1.5 mL). A solution of FeCl₃ (28.4 mg, 180 μmol) and DDQ (40.0 mg, 180 μmol) in MeNO₂ (0.5 mL) was added slowly to the mixture. The mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ solution. The organic phase was separated and washed with water and brine, and dried over anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography eluting with CH₂Cl₂/hexane. Recrystallization from CH₂Cl₂/methanol gave 2f (12.2 mg, 10.8 μmol, 61%).

**2f:** H NMR (600 MHz, CDCl₃, 25 °C): δ = 8.69 (d, J = 5.0 Hz, 2H, β), 8.54 (d, J = 5.0 Hz, 2H, β), 7.79 (d, J = 1.9 Hz, 2H, Ar), 7.75 (d, J = 1.9 Hz, 2H, Ar), 7.32-7.65 (m, 7H, β + Ar + Ph), 7.48 (t, J = 7.8 Hz, 2H, Ph), 7.38 (t, J = 7.8 Hz, 4H,
$^{1}H$ NMR (151 MHz, CDCl$_3$, 25 °C): δ = 155.21, 151.82, 149.99, 149.70 (d, $J$ = 14.4 Hz), 148.06, 146.75, 146.34, 144.55, 139.69, 137.96 (d, $J$ = 105.5 Hz), 136.58, 135.21, 133.47, 131.80 (d, $J$ = 8.7 Hz), 131.54, 130.52, 129.15, 128.79 (d, $J$ = 11.6 Hz), 128.25, 127.27, 123.80, 121.84, 120.82, 117.39, 103.46 (d, $J$ = 111.3 Hz), 35.41, 35.17, 35.12, 31.77, 31.30, and 29.15 ppm; $^{13}C$ NMR (151 MHz, CDCl$_3$, 25 °C): δ = 155.21, 151.82, 149.99, 149.70 (d, $J$ = 14.4 Hz), 148.06, 146.75, 146.34, 144.55, 139.69, 137.96 (d, $J$ = 105.5 Hz), 136.58, 135.21, 133.47, 131.80 (d, $J$ = 8.7 Hz), 131.54, 130.52, 129.15, 128.79 (d, $J$ = 11.6 Hz), 128.25, 127.27, 123.80, 121.84, 120.82, 117.39, 103.46 (d, $J$ = 111.3 Hz), 35.41, 35.17, 35.12, 31.77, 31.30, and 29.15 ppm; APCI-TOF-MS: $m/z$ = 1126.5180. Calcd for C$_{74}$H$_{77}$N$_4$58NiOP: 1126.5194 [M]

$^{1}H$ NMR spectrum of 2f in CDCl$_3$ at 25 °C. *Solvent and impurities.

$^{13}C$ NMR spectrum of 2f in CDCl$_3$ at 25 °C. *Solvent.
**Synthesis of 2c:** A flask containing 1g (19.0 mg, 18 µmol) was purged with argon, and then charged with CHCl₃ (1.5 mL). A solution of FeCl₃ (28.4 mg, 180 µmol) and DDQ (40 mg, 180 µmol) in MeNO₂ (0.5 mL) was added slowly to the mixture. The mixture was stirred at room temperature for 4 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ solution. The organic phase was separated and washed with water and brine, and dried over anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residue was charged with N-chlorosuccinimide (2.7 mg, 20 µmol), CuCl (2.0 mg, 20 µmol), DMF (2.0 mL), and toluene (1.0 mL). The mixture was stirred at 80 °C for 1 h. The reaction was quenched with a sufficient amount of aqueous Na₂S₂O₅ solution, extracted with CHCl₃, washed with H₂O twice and brine, and dried over anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography eluting with CHCl₃/hexane. Recrystallization from CHCl₃/methanol gave 2c (6.4 mg, 6.7 µmol, 37%).
2c: H NMR (600 MHz, CDCl₃, 25 °C): δ = 9.01 (d, J = 5.0 Hz, 2H, β), 8.83 (d, J = 5.0 Hz, 2H, β), 7.90 (d, J = 1.8 Hz, 2H, Ar), 7.77 (d, J = 1.8 Hz, 2H, Ar), 7.73 (s, 2H, β), 7.68 (t, J = 1.8 Hz, 1H, Ar), 7.06 (d, J = 1.8 Hz, 2H, Ar), 1.55 (s, 18H, tert-butyl), 1.51 (s, 18H, tert-butyl), and 1.47 (s, 18H, tert-butyl) ppm; ¹³C NMR (151 MHz, CDCl₃, 25 °C): δ = 154.59, 152.00, 149.76, 148.90, 147.75, 146.83, 145.73, 145.33, 141.47, 136.94, 133.14, 132.59, 129.55 (overlap), 128.01, 127.52, 127.15, 123.41, 121.62, 120.71, 116.62, 35.41, 35.20, 35.12, 31.81, 31.34, and 29.23 ppm; APCI-TOF-MS: m/z = 960.4414. Calcd for C₆₂H₆₇ClNiN₄S₅: 960.4413 [M]; UV/Vis (CH₂Cl₂): λmax (ε [M cm⁻¹]) = 399 (3.66 × 10⁴), 438 (5.07 × 10⁴), 510 (4.62 × 10⁴), 688 (4.95 × 10⁴), 741 (3.50 × 10⁴), and 825 nm (1.66 × 10⁴).

Figure S 13. H NMR spectrum of 2c in CDCl₃ at 25 °C. *Solvent and impurities.

Figure S 14. ¹³C NMR spectrum of 2c in CDCl₃ at 25 °C. *Solvent.
**Figure S 15.** Observed (top) and simulated (bottom) HR-APCI-TOF MS of 2c.

**Figure S 16.** UV/Vis absorption spectrum of 2c in CH₂Cl₂.

**Synthesis of 5Ni:** A flask containing 2c (22.5 mg, 23 μmol) and Ni(cod)₂ (38.6 mg, 138 μmol) was purged with argon, and then charged with DMF (8.0 mL) and 1,5-cyclooctadiene (34 μL, 138 μmol). The mixture was stirred at 100 °C for 9 h. The reaction mixture was diluted with CH₂Cl₂, washed with HO twice and then with brine, and dried over anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography eluting with CH₂Cl₂/hexane and gel permeation chromatography (GPC) eluting with toluene. Recrystallization from CH₂Cl₂/methanol gave 5Ni (18.0 mg, 9.7 μmol, 83%).

5Ni: H NMR (600 MHz, CDCl₃, 25 °C): δ = 8.68 (d, J = 5.0 Hz, 4H, β), 7.88-7.84 (m, 12H, Ar + β), 7.73-7.70 (m, 6H, Ar + β), 7.06 (s, 4H, Ar), 1.65 (s, 36H, tert-butyl), 1.55 (s, 36H, tert-butyl), and 1.37 (s, 36H, tert-butyl) ppm; ¹³C NMR (151 MHz, CDCl₃, 25 °C): δ = 154.99, 151.86, 150.48, 149.78, 148.97, 147.23, 146.69, 145.29, 141.33, 137.16, 135.80, 133.80, 129.64, 128.51, 127.08 (overlap), 123.26, 121.63, 120.71, 117.05, 116.34, 35.46, 35.17, 35.14, 31.25, 29.86, and
29.28 ppm; APCI-TOF-MS: \( m/z = 1850.9366 \). Calcd for \( \text{C}_{124}\text{H}_{134}\text{N}_{58}\text{Ni}_{2} \): 1850.9444 [M] ; UV/Vis (CHCl\(_3\)): \( \lambda_{\text{max}} \) (\( \epsilon \) [M cm\(^{-1}\)]) = 437 (1.39 \( \times \) 10\(^5\)), 512 (1.44 \( \times \) 10\(^5\)), 694 (1.43 \( \times \) 10\(^5\)), 750 (1.51 \( \times \) 10\(^5\)), and 824 nm (1.24 \( \times \) 10\(^5\)).

**Figure S 17.** H NMR spectrum of \( 5\text{Ni} \) in CDCl\(_3\) at 25 °C. *Solvent and impurities.

**Figure S 18.** C NMR spectrum of \( 5\text{Ni} \) in CDCl\(_3\) at 25 °C. *Solvent.

**Figure S 19.** Observed (top) and simulated (bottom) HR-APCI-TOF MS of \( 5\text{Ni} \).
Figure S 20. UV/Vis absorption spectrum of 5Ni in CHCl.

Synthesis of 5Zn: Conc. HSO₄ (0.8 mL) was added slowly to a mixture of 5Ni (11.2 mg, 6.0 μmol) and TFA (3.2 mL) at 0 °C. The reaction mixture was stirred at 0 °C in air for 30 min, and then poured into water at 0 °C. After neutralization by NaOH and K₂CO₃ at 0 °C, the product was extracted with CH₂Cl₂, washed with brine, and dried over anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residue was dissolved in CH₂Cl₂, and charged with an excess amount of Zn(OAc)₂·2H₂O dissolved in MeOH. The mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography eluting with CH₂Cl₂/hexane. Recrystallization from CHCl₃/methanol gave 5Zn (9.6 mg, 5.2 μmol, 85%).

5Zn: ¹H NMR of 5Zn with 2 equivalents of pyridine (600 MHz, CDCl₃, 25 °C): δ = 8.57 (d, J = 5.0 Hz, 4H, β), 7.93 (d, J = 1.9 Hz, 4H, Ar), 7.91 (d, J = 1.9 Hz, 4H, Ar), 7.72 (s, 4H, β), 7.70 (t, J = 1.9 Hz, 2H, Ar), 7.40 (d, J = 5.0 Hz, 4H, β), 7.12 (t, J = 7.8 Hz, 2H, pyridine), 6.98 (s, 4H, Ar), 6.50 (t, J = 7.8 Hz, 4H, pyridine), 5.25 (br-s, 4H, pyridine), 1.63 (s, 36H, tert-butyl), 1.57 (s, 36H, tert-butyl), and 1.38 (s, 36H, tert-butyl) ppm; ¹³C NMR of 5Zn with 2 equivalents of pyridine (151 MHz, CDCl₃, 25 °C): δ = 162.23, 156.05, 155.20, 151.78, 151.51, 149.28, 147.13, 146.56, 145.79, 145.28, 138.89, 137.00, 135.15, 134.61, 130.84, 130.55, 126.90, 126.20, 123.70, 122.61, 120.96, 120.58, 118.25, 117.28, 35.46, 35.14, 35.05, 31.93, 31.24, and 29.33 ppm; APCI-TOF-MS: m/z = 1862.9249. Calcd for C₁24H₁34N₈Zn₂: [M] – 1862.9320 [M]; UV/Vis (CHCl₃): λₘₐₓ (ε [M·cm⁻¹]) = 426 (9.51 × 10⁴), 487 (1.30 × 10⁵), 780 (1.54 × 10⁴), and 836 nm (1.05 × 10⁴); UV/Vis (CHCl₃ + pyridine 1%): λₘₐₓ (ε [M·cm⁻¹]) = 430 (8.11 × 10⁴), 487 (1.14 × 10⁵), 534 (1.01 × 10⁵), 616 (3.31 × 10⁴), 789 (1.67 × 10⁵), and 855 nm (1.26 × 10⁵).
Figure S21. $^1$H NMR spectrum of $\text{5Zn}$ in CDCl$_3$ at 25 °C. *Solvent and impurities.

Figure S22. $^{13}$C NMR spectrum of $\text{5Zn}$ in CDCl$_3$ at 25 °C. *Solvent.

Figure S23. Observed (top) and simulated (bottom) HR-APCI-TOF MS of $\text{5Zn}$. 
**Figure S 24.** UV/Vis absorption spectrum of 5Zn in CHCl.

**Figure S 25.** UV/Vis absorption spectrum of 5Zn in CHCl containing 1% of pyridine.

**Synthesis of 6:** A flask containing 5Zn (11.2 mg, 6.0 µmol), DDQ (6.8 mg, 30 µmol), and Sc(OTf)$_3$ (14.8 mg, 30 µmol) was purged with argon, and then charged with toluene (3.0 mL). The mixture was stirred at 70 °C for 1 h. The reaction mixture was filtered through a small plug of alumina with copious washings (THF). After removal of the solvent *in vacuo*, the residue was separated by silica gel chromatography eluting with CHCl/hexane/pyridine. Recrystallization from CHCl/methanol gave 6 (6.7 mg, 3.6 µmol, 60%).

6: H NMR (600 MHz, pyridine-d$_5$, 25 °C): $\delta$ = 8.19 (s, 4H), 8.06 (s, 4H), 8.00 (d, $J = 1.9$ Hz, 4H), 7.86 (t, $J = 1.9$ Hz, 2H), 7.33 (s, 4H), 7.29 (s, 4H), 1.57 (s, 36H), 1.47 (s, 36H), and 1.46 (s, 36H) ppm; (The signals for the carbons of 6 are unobservable because of the low solubility.); APCI-TOF-MS: $m/z$ = 1858.8967. Calcd for C$_{124}$H$_{130}$N$_8$Zn$_2$: 1858.9007 [M]
UV/Vis/NIR (CHCl₃ + pyridine 1%): λₚ (ε [M·cm⁻¹]) = 476 (1.02 × 10), 565 (4.11 × 10), 611 (3.73 × 10), 661 (2.58 × 10), 851 (4.42 × 10), and 1358 nm (1.88 × 10).

*Figure S 26.* H NMR spectrum of 6 in pyridine-d₅ at 25 °C. *Solvent and impurities.

*Figure S 27.* Observed (top) and simulated (bottom) HR-APCI-TOF MS of 6.

*Figure S 28.* UV/Vis absorption spectrum of 6 in CHCl₃ containing 1% of pyridine.
Synthesis of 8Ni: A flask containing 2c (9.6 mg, 10 μmol), Pd(dba)3 (2.3 mg, 2.5 μmol), and Sphos (2.1 mg, 5.0 μmol) was purged with argon, and then charged with toluene (2.0 mL), NEt3 (14 μL, 0.1 mmol), and HCOOH (4 μL, 0.1 mmol). The mixture was stirred at 120 °C for 13 h. The reaction mixture was diluted with CH2Cl2 and filtered through a small plug of silica gel with copious washings (CH2Cl2). After removal of the solvent in vacuo, the residue was separated by silica gel chromatography eluting with CH2Cl2/hexane to afford 8Ni. Recrystallization from CH2Cl2/methanol gave 8Ni (8.1 mg, 8.7 μmol, 87%).

8Ni: 1H NMR (600 MHz, CDCl3, 25 °C): δ = 8.72 (d, J = 5.1 Hz, 2H, β), 8.45 (s, 1H, meso), 8.33 (d, J = 5.1 Hz, 2H, β), 7.87 (d, J = 1.4 Hz, 2H, Ar), 7.86 (d, J = 1.4 Hz, 2H, Ar), 7.79 (s, 2H, β), 7.71 (t, J = 1.4 Hz, 1H, Ar), 7.06 (d, J = 1.4 Hz, 2H, Ar), 1.59 (s, 18H, tert-butyl), 1.55 (s, 18H, tert-butyl), and 1.47 (s, 18H, tert-butyl) ppm; 13C NMR (151 MHz, CDCl3, 25 °C): δ = 154.42, 151.55, 149.63, 149.05, 146.64, 146.53, 146.42, 144.93, 141.09, 137.36, 134.19, 133.36, 129.72, 127.91, 126.95, 126.69, 123.06, 121.50, 120.47, 115.52, 105.01 35.43, 35.17, 35.15, 31.88, 31.39, and 29.32 ppm; APCI-TOF-MS: m/z = 926.4816. Calcd for C62H68N458Ni: 926.4803 [M]–; UV/Vis (CH2Cl2): λmax (ε[M cm–1]) = 387 (3.89 × 104), 439 (6.35 × 104), 504 (6.68 × 104), 614 (4.44 × 104), 674 (5.77 × 104), 720 (4.30 × 104), and 812 nm (2.18 × 104).

Figure S 29. 1H NMR spectrum of 8Ni in CDCl at 25 °C. *Solvent and impurities.
Figure S 30. C NMR spectrum of 8Ni in CDCl at 25 °C. *Solvent.

Figure S 31. Observed (top) and simulated (bottom) HR-APCI-TOF MS of 8Ni.

Figure S 32. UV/Vis absorption spectrum of 8Ni in CHCl.
Synthesis of 8Zn: Conc. HSO₄ (2.0 mL) was added slowly to a mixture of 8Ni (8.4 mg, 9.1 μmol) and TFA (2.0 mL) at 0 °C. The reaction mixture was stirred at 0 °C in air for 2 h, and then poured into water at 0 °C. After neutralization by K₂CO₃ at 0 °C, the product was extracted with CH₂Cl₂, washed with brine, and dried over anhydrous Na₂SO₄. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography eluting with CH₂Cl₂/hexane. After removal of the solvent in vacuo, the residue was dissolved in CH₂Cl₂, and charged with an excess amount of Zn(OAc)₂·2H₂O dissolved in MeOH. The mixture was stirred for 40 min at room temperature. After removal of the solvent in vacuo, the residue was separated by silica gel chromatography eluting with CH₂Cl₂/hexane. Recrystallization from CH₂Cl₂/MeCN gave 8Zn (1.8 mg, 1.9 μmol, 21%).

8Zn: 1H NMR (600 MHz, CDCl₃, 25 °C): δ = 8.81 (d, J = 4.6 Hz, 2H, β), 8.55 (s, 1H, meso), 8.44 (d, J = 4.6 Hz, 2H, β), 7.95 (d, J = 1.8 Hz, 2H, Ar), 7.93 (d, J = 1.8 Hz, 2H, Ar), 7.73 (s, 2H, β), 7.71 (t, J = 1.8 Hz, 1H, Ar), 7.02 (d, J = 1.8 Hz, 2H, Ar), 1.62 (s, 18H, tert-butyl), 1.57 (s, 18H, tert-butyl), and 1.49 (s, 18H, tert-butyl) ppm; 13C NMR (151 MHz, CDCl₃, 25 °C): δ = 161.05, 154.71, 151.61, 151.06, 150.92, 149.50, 146.69, 146.62, 145.38, 138.52, 134.21, 133.45, 130.64, 130.28, 126.96, 126.83, 123.07, 121.18, 120.65, 116.25, 104.39, 35.44, 35.17, 35.13, 31.95, 31.37, and 29.36 ppm; APCI-TOF-MS: m/z = 932.4734. Calcd for C₆₂H₆₈N₄: 932.4741 [M]; UV/Vis/NIR (CHCl₃ + pyridine 1%): λmax (ε [M cm⁻¹]) = 426 (5.05 × 10⁴), 503 (5.51 × 10⁴), 528 (5.30 × 10⁴), 596 (6.13 × 10⁴), and 768 nm (6.84 × 10⁴).

Figure S33. 1H NMR spectrum of 8Zn in CDCl₃ at 25 °C. *Solvent and impurities.
Figure S34. $^{13}$C NMR spectrum of 8Zn in CDCl$_3$ at 25 °C. *Solvent.

Figure S35. Observed (top) and simulated (bottom) HR-APCI-TOF MS of 8Zn.

Figure S36. UV/Vis absorption spectrum of 8Zn in CHCl$_3$ containing 1% of pyridine.
4. X-Ray Crystal Structures

Figure S37. X-Ray crystal structure of 2e. (a) Top view and (b) side view. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules and all hydrogen atoms are omitted for clarity.

Figure S38. X-Ray crystal structure of 3. (a) Top view and (b) side view. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules and all hydrogen atoms are omitted for clarity.
Figure S 39. X-Ray crystal structure of 2f. (a) Top view and (b) side view. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules and all hydrogen atoms are omitted for clarity.

Figure S 40. X-Ray crystal structure of 6. (a) Top view and (b) side view. Thermal ellipsoids are shown at the 50% probability level. Solvent molecules, pyridine ligands, and all hydrogen atoms are omitted for clarity.
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<th>6</th>
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<td><strong>Fw</strong></td>
<td>1269.82</td>
<td>1067.05</td>
<td>1128.08</td>
<td>2349.63</td>
</tr>
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<td><strong>Crystal System</strong></td>
<td>Orthorhombic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>Pbcn (No. 60)</td>
<td>P-1 (No. 2)</td>
<td>P2$_1$/n (No. 14)</td>
<td>P-1 (No. 2)</td>
</tr>
<tr>
<td><strong>a</strong></td>
<td>11.0983(14) Å</td>
<td>14.734(6) Å</td>
<td>12.3714(16) Å</td>
<td>10.0013(12) Å</td>
</tr>
<tr>
<td><strong>b</strong></td>
<td>34.992(5) Å</td>
<td>20.554(8) Å</td>
<td>28.233(3) Å</td>
<td>14.5831(10) Å</td>
</tr>
<tr>
<td><strong>c</strong></td>
<td>32.965(4) Å</td>
<td>20.788(9) Å</td>
<td>41.360(6) Å</td>
<td>24.366(4) Å</td>
</tr>
<tr>
<td><strong>α</strong></td>
<td>90°</td>
<td>90.073(8)°</td>
<td>90°</td>
<td>75.428(16)°</td>
</tr>
<tr>
<td><strong>β</strong></td>
<td>90°</td>
<td>103.209(15)°</td>
<td>96.168(4)°</td>
<td>87.017(19)°</td>
</tr>
<tr>
<td><strong>γ</strong></td>
<td>90°</td>
<td>109.518(5)°</td>
<td>90°</td>
<td>71.26(2)°</td>
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<tr>
<td><strong>Volume</strong></td>
<td>12802(3) Å$^3$</td>
<td>5756(4) Å$^3$</td>
<td>14363(3) Å$^3$</td>
<td>3255.8(8) Å$^3$</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>8</td>
<td>2</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td><strong>Density (calcd.)</strong></td>
<td>1.318 g/cm$^3$</td>
<td>1.231 g/cm$^3$</td>
<td>1.174 g/cm$^3$</td>
<td>1.199 g/cm$^3$</td>
</tr>
<tr>
<td><strong>Completeness</strong></td>
<td>0.992</td>
<td>0.970</td>
<td>0.988</td>
<td>0.973</td>
</tr>
<tr>
<td><strong>Goodness-of-fit (all data)</strong></td>
<td>1.047</td>
<td>1.097</td>
<td>1.036</td>
<td>1.018</td>
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<tr>
<td><strong>R (I&gt;2σ(I))</strong></td>
<td>0.0921</td>
<td>0.1419</td>
<td>0.0739</td>
<td>0.0531</td>
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<tr>
<td><strong>wR (all data)</strong></td>
<td>0.2889</td>
<td>0.3713</td>
<td>0.2350</td>
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<tr>
<td><strong>CCDC No.</strong></td>
<td>1433487</td>
<td>1433488</td>
<td>1433489</td>
<td>1433486</td>
</tr>
</tbody>
</table>
5. DFT Calculations

The energy calculations of 6 and 7 were carried out using the Gaussian 09 program. 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, employing basis sets 6-31G(d) for C, H, and N and LANL2DZ for Zn. tert-Butyl groups of non-fused 3,5-di-tert-butylphenyl groups were replaced with hydrogen atoms to simplify the calculations.

Figure S41. Energy diagram of 6 and 7.
**Figure S 42.** Kohn-Sham orbital representations of 6.

**Figure S 43.** Kohn-Sham orbital representations of 7.

**Figure S 44.** Oscillator strength and simulated UV/Vis/NIR absorption spectra of 6 and 7.
**Table S 2. Selected oscillator strengths and their orbital compositions of 7.**

<table>
<thead>
<tr>
<th>wavelength (nm)</th>
<th>oscillator strength</th>
<th>orbital composition</th>
<th>oscillator strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>923.48</td>
<td>0.3302</td>
<td>HOMO to LUMO</td>
<td>0.65926</td>
</tr>
<tr>
<td>558.79</td>
<td>0.2856</td>
<td>HOMO−1 to LUMO+1</td>
<td>0.23175</td>
</tr>
<tr>
<td>515.49</td>
<td>1.7790</td>
<td>HOMO−4 to LUMO</td>
<td>0.48175</td>
</tr>
<tr>
<td>504.90</td>
<td>0.1853</td>
<td>HOMO−4 to LUMO</td>
<td>0.49990</td>
</tr>
<tr>
<td>413.90</td>
<td>0.1419</td>
<td>HOMO−2 to LUMO+2</td>
<td>0.36128</td>
</tr>
<tr>
<td>385.88</td>
<td>0.2671</td>
<td>HOMO−1 to LUMO+1</td>
<td>0.59574</td>
</tr>
</tbody>
</table>

**Table S 3. Selected oscillator strengths and their orbital compositions of 6.**

<table>
<thead>
<tr>
<th>wavelength (nm)</th>
<th>oscillator strength</th>
<th>orbital composition</th>
<th>oscillator strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1102.77</td>
<td>0.1482</td>
<td>HOMO to LUMO</td>
<td>0.62103</td>
</tr>
<tr>
<td>770.62</td>
<td>0.7594</td>
<td>HOMO−1 to LUMO+1</td>
<td>0.39574</td>
</tr>
<tr>
<td>676.97</td>
<td>0.2336</td>
<td>HOMO to LUMO+2</td>
<td>0.51821</td>
</tr>
<tr>
<td>593.61</td>
<td>0.1573</td>
<td>HOMO−2 to LUMO+2</td>
<td>0.60516</td>
</tr>
<tr>
<td>543.89</td>
<td>0.5493</td>
<td>HOMO−4 to LUMO+1</td>
<td>0.37011</td>
</tr>
<tr>
<td>505.87</td>
<td>0.5057</td>
<td>HOMO−7 to LUMO</td>
<td>0.61464</td>
</tr>
</tbody>
</table>
The calculations of dicationic triplet states of 1e, 1f, and 1h, and radical cation and dicationic singlet state of 1e were carried out using the Gaussian 09 program. 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, employing basis sets 6-31G(d). tert-Butyl groups were replaced with hydrogen atoms to simplify the calculations.

*Figure S 45.* Total spin density of radical cations of (a) 1e, (b) 1h, and (c) 4 (isovalue: 0.001).

*Figure S 46.* Kohn-Sham orbital representations of radical cation of 1e.

*Figure S 47.* Kohn-Sham orbital representations of dicationic singlet state of 1e.
Figure S 48. Kohn-Sham orbital representations of radical cation of 1h.

Figure S 49. Kohn-Sham orbital representations of dicaticonic singlet state of 1h.

Figure S 50. Selected charge distributions of radical cations and dications of 1e and 1h.
6. Femtosecond Transient Absorption Measurements

Figure S51. Femtosecond transient absorption spectra and decay profiles (inset) of (a) 8Zn, (b) 5Zn, and (c) 6 in toluene containing 1% of pyridine with photoexcitation at 800 nm (for 8Zn and 5Zn), and 1350 nm (for 6).
7. TPA Spectra and Z-Scan Curves

Figure S52. (a) One-photon absorption (black) and TPA spectrum (blue) of $8\text{Zn}$. (b) Z-scan curves of $8\text{Zn}$ by photoexcitations in the range from 1400 to 1700 nm in toluene containing 1% of pyridine. The TPA spectra are displayed at $\lambda_{ex}/2$ for comparison with the OPA spectra.

Figure S53. (a) One-photon absorption (black) and TPA spectrum (blue) of $5\text{Zn}$. (b) Z-scan curves of $5\text{Zn}$ by photoexcitations in the range from 1400 to 1800 nm in toluene containing 1% of pyridine. The TPA spectra are displayed at $\lambda_{ex}/2$ for comparison with the OPA spectra.
Figure S 54. (a) One-photon absorption (black) and TPA spectrum (blue) of 6. (b) Z-scan curves of 6 by photoexcitations in the range from 1600 to 1900 nm in toluene containing 1% of pyridine. The TPA spectra are displayed at $\lambda_{ex}$/2 for comparison with the OPA spectra.

Figure S 55. (a) One-photon absorption (black) and TPA spectrum (blue) of 7. (b) Z-scan curves of 7 by photoexcitations in the range from 1800 to 2400 nm in toluene containing 1% of pyridine. The TPA spectra are displayed at $\lambda_{ex}$/2 for comparison with the OPA spectra.
8. NICS Calculations and ACID Plot

Figure S 56. Calculated NICS(0) positions of (a) ZnTPP, (b) 8Zn, (c) 5Zn, (d) and 6.

Table S 4. Calculated NICS(0) values at the positions (Figure S 50) of ZnTPP, 8Zn, 5Zn, and 6

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP</td>
<td>-16.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8Zn</td>
<td>-12.3</td>
<td>-9.7</td>
<td>-11.4</td>
<td>17.0</td>
</tr>
<tr>
<td>5Zn</td>
<td>-11.7</td>
<td>-9.3</td>
<td>-9.8</td>
<td>17.0</td>
</tr>
<tr>
<td>6</td>
<td>-4.3</td>
<td>-1.7</td>
<td>-5.9</td>
<td>11.7</td>
</tr>
</tbody>
</table>
Figure S 57. Anisotropy of induced current density (ACID) plot for $\text{8Zn}$ at an isosurface value of 0.05 at the B3LYP/6-31G(d) level.
9. Electrochemical Properties

Cyclic voltammograms and differential pulse voltammograms were obtained under the following conditions; solvent: CH₂Cl₂ containing 1% pyridine, electrolyte: 0.1 M nBu₄NPF₆, working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag/AgNO₃, scan rate: 0.05 mV/s.

Figure S 58. (a) Cyclic voltammograms and (b) differential pulse voltammograms of 8Zn.

Figure S 59. (a) Cyclic voltammograms and (b) differential pulse voltammograms of 5Zn.
Figure S60. (a) Cyclic voltammograms and (b) differential pulse voltammograms of 6.

Figure S61. (a) Cyclic voltammograms and (b) differential pulse voltammograms of 7.
10. References

[S1] SHELXL-97 and SHELXS-97, program for refinement of crystal structures from diffraction data, University of Goettingen, Göttingen (Germany); G. Sheldrick and T. Schneider, Methods Enzymol. 1997, 277, 319.
