SUPPORTING INFORMATION

Title: meso,meso-Linked and Triply Fused Diporphyrins with Mixed-Metal Ions: Synthesis and Electrochemical Investigations

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Experimental Section

4,15-Bis(3,5-dicyanophenyl)-10,20-bis[3,5-di(tert-butyl)phenyl]porphyrinato-
N^{21},N^{22},N^{23},N^{24}zinc(II) ((CN)$_4$ZnP 3): To a 250-mL round-bottomed flask under N$_2$
charged with 22$^{[39]}$ (764 mg, 8.7 × 10^{-1} mmol) in PhMe (200 mL) was added 23 (1200
mg, 4.6 mmol), [Pd(Ph$_3$P)$_4$] (105 mg, 9.0 × 10^{-2} mmol), and Cs$_2$CO$_3$ (4060 mg, 23
mmol). The mixture was degassed and heated to 140 °C for 20 h. Filtration through
Celite and evaporation of the solvent, followed by FC (SiO$_2$; cyclohexane/CH$_2$Cl$_2$ 1:2)
gave 3 (535 mg, 70%) as a red solid. M.p.: > 300 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ =
9.11 (d, $J$ = 4.8 Hz, 4 H), 8.74 (d, $J$ = 4.8 Hz, 4 H), 8.74 (d, $J$ = 1.5 Hz, 4 H), 8.38 (t, $J$ =
1.5 Hz, 2 H), 8.08 (d, $J$ = 1.8 Hz, 4 H), 7.86 (t, $J$ = 1.8 Hz, 2 H), 1.55 (s, 36 H); $^{13}$C
NMR (75.41 MHz, CDCl$_3$): $\delta$ = 151.47, 149.31, 149.22, 141.15, 140.40, 136.21,
134.32, 134.20, 131.06, 130.24, 124.46, 121.61, 117.08, 115.66, 112.88, 35.33, 31.97;
IR (neat): 2959 m, 2237 m, 1589 s, 1476 m, 1424 m, 1393 w, 1362 m, 1206 m, 1073 m, 1001 s, 936 s, 882 m, 822 m, 794 m, 715 m, 682 m; UV-Vis (CHCl$_3$):
427 (114500), 550 (5400), 591 (1100) nm; HR-FT-ICR-MALDI-MS (matrix: DCTB):
caled. for C$_{64}$H$_{56}$N$_8$Zn$^+$ ($M^+$): 1000.39; found: 1000.30.

15-Bis (3, 5-dicyanophenyl)-10, 20-bis [3, 5-di (tert-butyl) phenyl]porphyrin
((CN)$_4$H$_3$P 5): To a 100 mL round-bottom flask charged with 3 (50 mg, 5.0 × 10^{-2}
mmol) in CH$_2$Cl$_2$ (50 mL), TFA (10 mg, 8.5 × 10^{-2} mmol) was added at 0 °C. The
mixture was stirred for 2 h at 20 °C, then Et$_3$N (10 mL) was added dropwise. The color
of solution changed from green to red. The mixture was washed with water (3 × 50
mL), the organic phase dried (Na$_2$SO$_4$), and the solvent evaporated in vacuo. FC (SiO$_2$;
cyclohexane/CH$_2$Cl$_2$ 1: 2) gave 5 (47 mg, quant.) as a dark solid. M.p.: > 300 °C. $^1$H
NMR (300 MHz, CDCl$_3$): $\delta$ = 9.16 (d, $J$ = 4.5 Hz, 4 H), 8.90 (d, $J$ = 1.5 Hz, 4 H), 8.80
(d, $J$ = 4.5 Hz, 4 H), 8.49 (t, $J$ = 1.5 Hz, 2 H), 8.23 (d, $J$ = 1.5 Hz, 4 H), 7.99 (t, $J$ = 1.5
Hz, 2 H), 1.70 (s, 36 H), –2.67 (s, 2 H); $^{13}$C NMR: $\delta = 149.54, 145.64, 145.58, 140.56, 136.07, 135.50, 134.89, 134.81, 133.50, 130.53, 130.47, 130.35, 129.72, 123.67, 123.60, 121.98, 121.89, 117.14, 117.09, 114.87, 113.19, 113.14, 35.41, 32.05; IR (neat): 2961 m, 2902 m, 2235 m, 1807 w, 1722 w, 1579 m, 1479 m, 1421 w, 1361 w, 1289 w, 1240 m, 1154 w, 1076 m, 1057 m, 979 m, 914 m, 901 m, 881 m, 819 m, 800 s, 733 m, 714 w, 678 m; UV-Vis (CHCl₃): 426 (117600), 519 (5400), 554 (2400), 593 (1800), 649 (1300) nm; HR-FT-ICR-MALDI-MS (matrix: DCTB): calcd. $^{15}$H$_{58}$N$_8$ (M$^+$): 938.49; found: 939.18.

15-Bis(3,5-dicyanophenyl)-10,20-bis[3,5-di(tert-butyl)phenyl]porphyrinato-N$^{21}$,N$^{22}$,N$^{23}$,N$^{24}$copper(II) ((CN)$_4$CuP 4): A saturated solution of Cu(OAc)$_2$ in 5 mL MeOH was added to a solution of 5 (30 mg, 3.2 × 10$^{-2}$ mmol) in 5 mL CHCl$_3$, and the resulting mixture was heated to reflux for 3 h in the dark to yield 4 (32 mg, quant.) as a red-brown solid. M.p.: > 300 °C; IR (neat): 2955 m, 2925 m, 2869 m, 2237 m, 1817 w, 1726 m, 1592 m, 1461 m, 1427 m, 1362 m, 1348 m, 1282 m, 1260 m, 1247 m, 1222 m, 1206 m, 1120 m, 1075 m, 1003 s, 935 s, 898 m, 881 m, 824 m, 800 s, 715 m, 687 m, 671 m, 605 m; UV/VIS (CHCl$_3$): 423 (111200), 542 (5700), 577 (1000) nm; HR-MALDI-MS (DCTB mix): calcd. for C$_{64}$H$_{56}$CuN$_8$ (M$^+$): 999.39; found: 1000.67.

3-(4, 4, 5, 5-Tetramethyl-3,2-dioxaborolan-2-yl) Isophthalonitrile (23): To a 50 mL, three-necked, round-bottomed flask, 5-bromoisophthalonitrile (536 mg, 2.6 mmol), bis(pinacolato)diboron (715 mg, 2.81 mmol), potassium acetate (765 mg, 7.8 mmol), palladium acetate (20 mg, 8.0 × 10$^{-2}$ mmol), and DMF (10 mL) were added. The mixture was degassed with N$_2$ for 30 min. It was then heated in an oil bath to 85 °C until completion of the reaction (ca. 5 h). The mixture was cooled to 20 °C and diluted with water (50 mL) to induce precipitation. The gray solid was collected by filtration, rinsed with water, and dried. It was dissolved in ethyl acetate (30 mL), and insoluble
material was removed by filtration through a pad of Celite. The filtrate yielded 23 as white solid. The mother liquor from the first filtration was extracted with ethyl acetate (50 mL) and dried (Na₂SO₄). Removal of the solvent yielded in additional product providing a combined yield of 362 mg (55 %). An analytically pure sample was obtained by recrystallization from ethyl acetate as light yellow solid. M.p. 45-47 °C; ¹H NMR (300 MHz, (CD₃)₂SO): δ = 8.76 (s, 2 H), 8.25 (s, 1 H), 1.31 (s, 12 H); ¹³C NMR (75.41 MHz, CDCl₃): δ = 143.60, 135.27, 116.8, 112.45, 87.12, 22.31.

5-Isophthalonitrile -10, 20-bis (3,5-di-(tert-butyl)phenyl) porphyrinato-N²¹, N²², N²³, N²⁴ zinc (II) (24): To a 250-mL round-bottomed flask under N₂ charged with 5-iodo-10, 20-bis(3,5-di-(tert-butyl)phenyl)porphyrinato-N²¹, N²², N²³, N²⁴ zinc(II)⁴ᵈ (764 mg, 8.7 × 10⁻¹ mmol) in PhMe (200 mL), 23 (582 mg, 2.3 mmol), [Pd(Ph₃P)₄] (105 mg, 9.0 × 10⁻² mmol), and Cs₂CO₃ (2030 mg, 11.5 mmol) were added. The mixture was degassed and heated to 140 °C for 20 h. Filtration through Celite, evaporation of the solvent, and FC (SiO₂; cyclohexane/CH₂Cl₂ 1:2) gave 24 (427 mg, 56%) as a red solid. M.p.: > 300 °C; ¹H NMR (300 MHz, CDCl₃): δ = 10.35 (s, 1 H), 9.46 (d, J = 4.5 Hz, 2 H), 9.20 (d, J = 4.5 Hz, 2 H), 9.13 (d, J = 3.9 Hz, 2 H), 8.74 (d, J = 3.9 Hz, 4 H), 8.36 (s, 1 H), 8.11 (d, J = 0.9 Hz, 4 H), 7.85 (t, J = 0.9 Hz, 2 H), 1.56 (s, 36 H); ¹³C NMR (75.41 MHz, CDCl₃): δ = 151.02, 150.53, 150.39, 148.80, 148.31, 146.42, 141.24, 140.14, 134.02, 133.38, 132.24, 130.18, 129.99, 122.86, 121.13, 116.90, 114.88, 112.35, 107.35; IR (neat): 2956 m, 2234 w, 1590 m, 1463 m, 1362 s, 1211 m, 1143 s, 1062 m, 999 m, 968 m, 919 w, 870 w, 847 m, 818 m, 792 m, 714 m, 689 m, 643 w; UV-Vis (CHCl₃): 424 (176600), 552 (7800), 591 (5300) nm; HR-MALDI-MS (DCTB mix): calcd. for C₅₆H₄₄N₆Zn⁺ (M⁺): 874.37; found: 874.37.

1-Iodo-5- isophthalonitrile -10, 20-bis (3,5-di-(tert-butyl)phenyl)porphyrinato N²¹, N²², N²³, N²⁴ zinc (II) (25): To a 100 mL round-bottom flask, charged with 24 (200
mg, 2.3 × 10⁻¹ mmol) in CHCl₃/pyridine 60:1 (65 mL), I₂ (30 mg, 2.3 × 10⁻¹ mmol) and a solution of AgPF₆ (58 mg, 2.3 × 10⁻¹ mmol) in CH₃CN (5 mL) were added. The reaction was monitored by TLC (cyclohexane/CH₂Cl₂ 1:2) and was complete within 11 min at 20 °C. After addition of water (20 mL), the phases were separated. The organic layer was washed with water (3 × 50 mL) and dried (Na₂SO₄), and the solvent was evaporated. FC (SiO₂; cyclohexane/CH₂Cl₂ 1:2) provided 1-Iodo-5- isophthalonitrile -10, 20- bis (3,5-di-(tert-butyl)phenyl)porphyrinato N²¹, N²², N²³, N²⁴ zinc (II) (25) as a red solid. M.p.: > 300 °C; ¹H NMR (300 MHz, CDCl₃): δ = 9.84 (d, J = 5.1 Hz, 2 H), 9.05 (d, J = 4.8 Hz, 2 H), 9.02 (d, J = 1.5 Hz, 2 H), 8.70 (d, J = 1.5 Hz, 2 H), 8.67 (d, J = 5.1 Hz, 2 H), 8.34 (t, J = 1.5 Hz, 1 H), 8.05 (d, J = 1.2 Hz, 4 H), 7.85 (t, J = 1.5 Hz, 2 H), 1.56 (s, 36 H); ¹³C NMR (75.41 MHz, CDCl₃): δ = 152.27, 152.01, 150.83, 148.98, 148.74, 145.99, 140.97, 140.02, 138.13, 134.22, 134.08, 133.73, 130.52, 129.84, 124.03, 121.23, 116.77, 115.05, 112.46, 35.23, 31.91; IR (neat): 2595m, 2359w, 2236w, 1791w, 1589s, 1519w, 1475m, 1423w, 1361m, 1322m, 1288m, 1246m, 1205w, 1071m, 1045w, 998s, 950m, 929m, 898m, 881m, 815m, 792s, 783m, 716m, 693s; UV-Vis (CHCl₃): 432 (165400), 564 (6500), 608 (3400) nm; HR-MALDI-MS (DCTB mix): calcd. for C₅₆H₅₄IN₆Zn⁺ (M⁺): 1000.27; found: 1000.27.

1-Iodo-5- isophthalonitrile -10, 20- bis (3,5-di-(tert-butyl)phenyl)porphyrin (26): To a 100 mL round-bottom flask, charged with 25 (50 mg, 5.0 × 10⁻² mmol) in CH₂Cl₂ (50 mL), TFA (10 mg, 8.5 × 10⁻² mmol) was added at 0 °C. The mixture was stirred for 2 h at 20 °C, the Et₃N (10 mL) was added dropwise. The color of the solution changed from green to red. The mixture was washed with water (3 × 50 mL), the organic phase dried (Na₂SO₄), and the solvent evaporated in vacuo. FC (SiO₂; cyclohexane/CH₂Cl₂ 1: 2) gave 26 (42 mg, 90%) as a dark solid. M.p. > 300 °C; ¹H NMR (300 MHz, CDCl₃): δ = 9.72 (d, J = 5.1 Hz, 2 H), 8.94 (d, J = 5.1 Hz, 2 H), 8.91
(d, $J = 5.1$ Hz, 2 H), 8.72 (d, $J = 1.5$ Hz, 2 H), 8.57 (d, $J = 5.1$ Hz, 2 H), 8.36 (t, $J = 1.5$ Hz, 1 H), 8.05 (d, $J = 1.5$ Hz, 4 H), 7.85 (t, $J = 1.5$ Hz, 2 H), 1.54 (s, 36 H), –2.70 (s, 2 H); $^{13}$C NMR (75.41 MHz, CDCl$_3$): $\delta = 148.93, 145.23, 140.35, 140.18, 134.33, 129.97, 123.17, 121.47, 116.76, 114.06, 112.82, 35.20, 31.86$; IR (neat): 2960m, 2359w, 2234w, 1790w, 1579m, 1475m, 1331m, 1234m, 1180w, 1080m, 966s, 914s, 899m, 81w, 818w, 788s, 167w, 715s, 687m; UV-Vis (CHCl$_3$): 426 (171100), 522 (7300), 558 (6700), 598 (5200), 655 (6300) nm; HR-MALDI-MS (DCTB mix): calcd. for C$_{56}$H$_{56}$IN$_6$ ($M^+$): 938.35; found: 938.35.

1-(4, 4, 5, 5-Tetramethyl-3, 2-dioxaborolan-2-yl) - 5- isophthalonitrile -10, 20-bis (3,5-di-(tert-butyl)phenyl) porphyrinato-N$^{21}$, N$^{22}$, N$^{23}$, N$^{24}$ zinc (II) (27): A 10 mL Schlenk flask was charged with 26 (25 mg, 2.0 $\times$ 10$^{-2}$ mmol), pinacolborane (24 µL, 1.7 $\times$ 10$^{-1}$ mmol), triethylamine (36 µL, 2.6 $\times$ 10$^{-1}$ mmol), [PdCl$_2$(PPh$_3$)$_2$] (1 mg, 1.0 $\times$ 10$^{-3}$ mmol), and of 1,2-dichloroethane (5 mL) under N$_2$. The mixture was stirred at 90 °C for 1 h, at which point TLC indicated complete consumption of starting material. Aqueous KCl (5 mL) was added and the mixture washed with water, then dried (MgSO$_4$). The solvent was evaporated and the purified by chromatography (SiO$_2$; cyclohexane/CH$_2$Cl$_2$ 1:2) to give 27 (22 mg, 90%) as a red solid. M.p.: > 300 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 9.94$ (d, $J = 4.8$ Hz, 2H), 9.17 (d, $J = 5.1$ Hz, 2 H), 9.08 (d, $J = 4.8$ Hz, 2 H), 8.72 (d, $J = 1.8$ Hz, 2 H), 8.70 (d, $J = 5.1$ Hz, 2 H), 8.35 (t, $J = 1.8$ Hz, 1 H), 8.09 (d, $J = 1.8$ Hz, 4 H), 7.84 (t, $J = 1.8$ Hz, 2 H), 1.86 (s, 12 H), 1.56 (s, 36 H). $^{13}$C NMR (75.41 MHz, CDCl$_3$): $\delta = 150.4, 149.5, 141.0, 139.2, 135.9, 133.9, 124.5, 122.1, 121.5, 120.7, 119.5, 115.5, 114.2, 113.2, 110.4, 83.9, 41.4, 31.3, 21.4; IR (neat): 2961m, 2360w, 2236w, 1724w, 1590m, 1528w, 1475m, 1318m, 1274s, 1247m, 1207m, 1143s, 1067m, 1051s, 1002s, 962w, 926m, 900m, 878m, 854m, 820m, 797m, 729w, 712s, 688m, 669m; UV-Vis (CHCl$_3$) 426 (203200), 554 (33100), 600 (7600)
nm; HR-MALDI-MS (DCTB mix): calcd. for C$_{62}$H$_{65}$BN$_6$O$_2$Zn$^+$ ($M^+$): 1000.46; found: 1000.45.

1- (4, 4, 5, 5-Tetramethyl-3, 2-dioxaborolan-2-yl) - 5- isophthalonitrile -10, 20- bis (3,5-di-(tert-butyl)phenyl) porphyrin (28): To a 100 mL round-bottom flask, charged with 27 (100 mg, 1.0 × 10$^{-1}$ mmol) in CH$_2$Cl$_2$ (75 mL), TFA (14 µl, 20 mg, 1.7 × 10$^{-1}$ mmol) was added dropwise. The mixture was stirred for 2 h at 20 °C, then Et$_3$N (15 mL) was added. The color of the solution changed from green to red. The mixture was washed with water (3 × 50 mL), the organic phase dried (Na$_2$SO$_4$), and the solvent evaporated in vacuo. FC (SiO$_2$; cyclohexane/CH$_2$Cl$_2$ 1: 2) gave 26 (94 mg, quant.) as a dark solid. M.p. > 300 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 9.87$ (d, $J = 4.8$ Hz, 2 H), 9.04 (d, $J = 4.8$ Hz, 2 H), 8.95 (d, $J = 4.8$ Hz, 2 H), 8.73 (d, $J = 1.5$ Hz, 2 H), 8.61 (d, $J = 4.8$ Hz, 2 H), 8.36 (t, $J = 1.5$ Hz, 1 H), 8.08 (d, $J = 1.8$ Hz, 4 H), 7.84 (t, $J = 1.8$ Hz, 2 H), 1.86 (s, 12 H), 1.56 (s, 36 H); HR-MALDI-MS (3-HPA): m/z calc. for C$_{62}$H$_{67}$BN$_6$O$_2$ $^+$: 938.54; found: 938.45.

1-Iodo-5- isophthalonitrile -10, 20- bis (3,5-di-(tert-butyl)phenyl)porphyrinato-N$_{21}$, N$_{22}$, N$_{23}$, N$_{24}$ copper (II) (30): A saturated solution of Cu(OAc)$_2$ in 5 mL MeOH was added to a solution of 26 (50 mg, 5.3 × 10$^{-2}$ mmol) in 5 mL CHCl$_3$, and the resulting mixture was heated to reflux for 3 h. 10 mL of CH$_2$Cl$_2$ were added, the mixture was washed with water (3 × 10 mL) and dried (MgSO$_4$), and the solvent evaporated to yield 29 (53 mg, quant.) as a red-brown solid. M.p. > 300 °C; HR-MALDI-MS (3-HPA): m/z calc. for C$_{63}$H$_{65}$BCuN$_6$O$_2$$^+$ ($M^+$): 999.46; found: 999.46.
mixture was heated to reflux for 3 h. After addition of 10 mL CH₂Cl₂, the mixture was washed with water (3 × 10 mL), dried (MgSO₄), and the solvent was evaporated to yield 29 (53 mg, quant.) as a red solid. M.p. > 300 °C; HR-MALDI-MS (DCTB mix): m/z calc. for C₅₆H₅₃CuIN₆⁺ (M⁺): 999.27; found: 999.27.