Syntheses and $^1$H NMR Spectroscopy of Rigid, Cofacially Aligned, Porphyrin-Bridge-Quinone Systems in which the Interplanar Separations Between the Porphyrin, Aromatic Bridge, and Quinone are Less than the Sum of Their Respective van der Waals Radii

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Experimental Section:
1-(2,5-Dimethoxyphenyl)-8-[2,5-dimethyl-4-(4′,4′,5′,5′-tetramethyl[1′,3′,2′]dioxaborolan-2′-yl]-1-phenyl]naphthalene (8b). A 50 mL Schlenk reaction vessel was charged with compound 7b (356 mg, 1.0 mmol), compound 3 (194 mg, 0.50 mmol), K$_3$PO$_4$ (164 mg, 0.77 mmol), and Pd(PPh$_3$)$_4$ (29 mg, 0.025 mmol). DMF (5 mL), that had previously been deoxygenated via three freeze-pump-thaw cycles, was cannula transferred to the tube containing the solids. The reaction was heated to 100 °C for 6 h, cooled, filtered, and partitioned with benzene and satd NaCl; the organic layer was washed with satd NaCl (3 x 75 mL) and H$_2$O (1 x 50 mL), following which it was dried over CaCl$_2$, filtered, and evaporated. The recovered solid was chromatographed on silica gel (CHCl$_3$) in order to remove excess 7b, which eluted just prior to the product. After removal of the volatiles, the collected product was rechromatographed on silica gel (5.7:1 hexanes:THF). The product was isolated
as an oil which solidified upon standing at room temperature; isolated yield = 222 mg (91% based on 194 mg of compound 3). *anti:syn* 1.6:1 $^1$H NMR (250 MHz, CDCl$_3$): δ 7.93-7.88 (m, 2 H), 7.52-7.44 (m, 2 H), 7.28-7.13 (m, 3 H), 6.82 (s', 1 H), 6.59 (s''), 1 H), 6.57 (d', 1 H, 3.0 Hz), 6.45 (d'', 1 H, J=3.0 Hz), 6.39 (dd'', 1 H, J=3.2 Hz, J=8.9 Hz), 6.37 (dd', 1 H, J=3.0 Hz, J=8.8 Hz), 6.29 (d', 1 H, 8.9 Hz), 6.22 (d'', 1 H, 8.9 Hz), 3.68 (s'', 3 H), 3.67 (s', 3 H), 3.51 (s', 3 H), 3.42 (s'', 3 H), 2.36 (s', 3 H), 2.28 (s'', 3 H), 1.90 (s'', 3 H), 1.77 (s', 3 H), 1.34 (s', 12 H), 1.33 (s'', 12 H). $^{13}$C NMR (500 MHz, CDCl$_3$): δ 19.55, 19.74, 21.35, 21.79, 24.72, 24.79, 24.91, 24.97, 54.85, 54.95, 55.18, 55.76, 82.97, 109.19, 109.94, 111.90, 112.65, 116.36, 118.21, 124.65, 124.79, 124.84, 124.90, 128.42, 128.76, 128.81, 129.20, 129.46, 130.07, 130.21, 130.24, 130.55, 130.65, 131.79, 131.81, 132.25, 132.41, 133.30, 134.56, 134.87, 136.33, 136.40, 136.58, 136.91, 139.74, 139.81, 140.09, 140.33, 144.18, 144.91, 150.30, 150.37, 152.25, 152.31. HRMS (Cl+) m/z: 494.2637 (calcd for C$_{32}$H$_{33}$BO$_4$ (M+) 494.2628).

1-(2,5-Dimethoxyphenyl)-8-[2,5-difluoro-4-(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl]-1-phenyl)naphthalene (8c). A 50 mL Schlenk reaction vessel was charged with 7c (182 mg, 0.50 mmol), 3 (129 mg, 0.33 mmol), K$_3$PO$_4$ (106 mg, 0.50 mmol), and Pd(PPh$_3$)$_4$ (19 mg, 0.016 mmol). DMF (10 mL), that had previously been deoxygenated via three freeze-pump-thaw cycles, was cannula transferred to the tube containing the solids. The reaction was heated to 100 °C for 1 h, cooled, filtered, and partitioned with benzene and satd NaCl; the organic layer was washed with satd NaCl (3 x 75 mL) and H$_2$O (1 x 50 mL), following which it was dried over CaCl$_2$, filtered, and evaporated. The recovered solid was chromatographed on silica.
gel (5.7:1 hexanes:THF); isolated yield = 78 mg (47% based on 129 mg of compound 3). 

$^1$H NMR (250 MHz, CDCl$_3$): δ 7.96 (d, 1 H, J=9.0 Hz), 7.93 (d, 1 H, J=8.3 Hz), 7.54 (t, 1 H, J=7.6 Hz), 7.50 (t, 1 H, J=8.3 Hz), 7.38-7.22 (m, 2 H), 6.91-6.76 (m, 3 H), 6.44 (dd, 1 H, J=3.5 Hz, J=9.0 Hz), 6.31 (d, 1 H, J=8.3 Hz), 3.73 (s, 3 H), 3.50 (s, 3 H), 1.37 (s, 12 H). $^{13}$C NMR (500 MHz, CDCl$_3$): δ 24.60, 24.64, 24.80, 24.89, 24.90, 54.92, 55.00, 55.81, 55.85, 83.91, 84.28, 109.55, 110.25, 113.17, 113.66, 116.79, 116.82, 117.00, 117.03, 117.97, 120.70, 120.77, 120.88, 120.96, 124.51, 124.69, 125.26, 125.35, 128.81, 128.99, 129.84, 129.89, 130.01, 130.32, 130.45, 130.83, 131.66, 132.83, 134.39, 136.35, 150.14, 150.68, 152.79, 152.84, 153.49, 155.41, 160.87, 162.83. $^{19}$F NMR (200 MHz, CDCl$_3$): δ -111.55 (s', 1 F), -112.10 (s', 1 F), -119.57 (d', 1 F, J=14.6 Hz), -123.30 (d'', 1 F, J=16.0 Hz). HRMS (Cl+) m/z: 503.2196 (calcd for C$_{30}$H$_{30}$BF$_2$O$_4$ (MH+) 503.2205).

1-Iodo-8-[2',5'-dimethyl-4'-(8''-[2''', 5'''-dimethoxyphenyl]-1''-naphthyl)-1'-phenyl]naphthalene (9b). A 25 mL Schlenk flask was charged 8b (15 mg, 0.030 mmol), 1,8-diiodonaphthalene (12 mg, 0.032 mmol), Ba(OH)$_2$·8H$_2$O (15 mg, 0.047 mmol), and Pd(PPh$_3$)$_4$ (2 mg, 0.002 mmol). A degassed solution of dimethoxyethane (DME) (3 mL) and distilled water (0.5 mL) was cannula transferred to the reaction vessel and the reaction was heated to 80 °C for 3.5 h. After the reaction was partitioned with benzene and satd NaCl, the organic layer was washed with satd NaCl (3 x 50 mL) and H$_2$O (1 x 50 mL), dried over CaCl$_2$, filtered, and evaporated. The recovered solid was chromatographed on silica gel (9:1 hexanes:THF); the product, isolated as an oil, solidified upon standing at room
temperature. Isolated yield = 12 mg (64% based on 15 mg of compound 9b). *anti*:syn  

1.8:1 $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.20 (d, 1 H, J=6.9 Hz), 7.99-7.85 (m, 4 H), 7.61-7.49 (m, 3 H), 7.38-7.27 (m, 3 H), 7.07 (t, 1 H, J=7.6 Hz), 6.90 (s, 1 H), 6.72-6.64 (m, 2 H), 6.58-6.56 (m, 1 H), 6.44 (dd, 1 H, J=4.0 Hz, J=8.8 Hz), 3.69 (s′, 3 H), 3.68 (s″, 3 H), 3.55 (s′, 3 H), 3.47 (s″, 3 H), 1.92 (s″, 3 H), 1.83 (s′, 3 H), 1.74 (s′, 3 H), 1.70 (s″, 3 H). $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 19.81, 19.82, 20.03, 20.24, 54.99, 55.04, 55.24, 55.71, 91.52, 91.59, 109.31, 109.95, 112.21, 112.87, 115.84, 118.02, 124.75, 124.78, 124.89, 124.91, 125.19, 125.21, 126.32, 128.40, 128.44, 128.91, 128.94, 128.96, 129.58, 129.73, 129.95, 129.97, 130.22, 130.39, 130.42, 130.50, 130.64, 130.68, 130.92, 131.09, 131.22, 131.82, 132.09, 132.24, 132.59, 132.80, 132.87, 132.99, 133.03, 133.07, 134.69, 134.97, 135.10, 135.16, 136.67, 136.94, 137.18, 137.55, 139.87, 139.89, 141.15, 141.18, 142.03, 142.25, 142.78, 150.70, 150.50, 152.26. HRMS (CI+) m/z: 620.1190 (calcd for C$_{36}$H$_{29}$IO$_2$ (M+).)  

1-Iodo-8-[2′,5′-difluoro-4′-(8″-[2″, 5″-dimethoxyphenyl]-1″-naphthyl)-1′-phenyl]naphthalene (9c). A 25 mL Schlenk flask was charged with 8c (46 mg, 0.092 mmol), 1,8-diiodonaphthalene (70 mg, 0.18 mmol), K$_2$PO$_4$ (29 mg, 0.14 mmol), and DMF (5 mL). The reaction mixture was degassed via three freeze-pump-thaw cycles, following which Pd(PPh$_3$)$_4$ (11 mg, 0.01 mmol) was added. The reaction was heated to 100 °C for 70 min. After partitioning the reaction mixture with CHCl$_3$ and H$_2$O, the organic layer was washed with H$_2$O (4 x 50 mL), dried over CaCl$_2$, filtered, and evaporated, leaving an oily yellow residue which was chromatographed on silica (3:1 hexanes:THF). Following addition of n-pentane to the recovered oil and cooling
to -38 °C, a white solid was isolated via vacuum filtration on a fine glass frit;

isolated yield = 38 mg (66% based on 46 mg of compound 9c). *anti:syn* 5.6:1 ¹H NMR (250 MHz, CDCl₃): δ 8.21 (d, 1 H, J=7.3 Hz), 8.01-7.89 (m, 4 H), 7.63-7.33 (m, 6 H), 7.10 (t, 1 H, J=7.7 Hz), 6.88 (dd, 1 H, J=6.1 Hz, J=9.4 Hz), 6.80-6.60 (m, 2 H), 6.55 (dd, 1 H, J=6.1 Hz, J=9.0 Hz), 6.44 (d, 1 H, J=8.7 Hz), 3.72 (s’, 3 H), 3.67 (s”, 3 H), 3.51 (s’, 3 H), 3.49 (s”, 3 H). ¹³C NMR (500 MHz, CDCl₃): δ 55.03, 55.14, 55.75, 55.77, 91.21, 91.24, 109.82, 110.25, 113.45, 113.97, 116.08, 116.75, 116.78, 116.95, 116.98, 117.36, 117.39, 117.56, 117.59, 118.35, 118.38, 118.55, 118.58, 118.75, 119.59, 119.62, 119.79, 119.82, 124.65, 124.79, 125.11, 125.14, 125.26, 125.30, 126.72, 126.74, 128.89, 129.11, 129.80, 129.98, 130.25, 130.28, 130.42, 130.56, 130.61, 130.75, 130.80, 130.94, 131.15, 131.41, 131.44, 132.19, 132.49, 132.73, 134.09, 134.16, 134.60, 134.91, 135.19, 135.28, 136.20, 136.32, 142.39, 142.41, 150.39, 150.99, 152.71, 152.73, 153.49, 153.51, 154.78, 154.80, 155.41, 155.42, 156.68, 156.7. ¹⁹F NMR (200 MHz, CDCl₃): δ -119.59 (m’, 1 F), -122.05 (m’, 1 F), -122.45 (m”, 1 F), -122.98 (m”, 1 F). HRMS (CI+) m/z: 629.0758 (calcd for C₃₄H₂₄F₂I₂O₂ (MH+) 629.0789).

[5-(8'-[2''',5'''-Dimethyl-4’’’-[8’’’-2’’’’, 5’’’-dimethoxyphenyl]-1’’’’-naphthyl]-1’’’’-phenyl]-1’-naphthyl)-10,20-diphenylporphinato]zinc(II) (10b). A 25 mL Schlenk tube was charged with 9b (42 mg, 0.068 mmol), [5-(4’,4’,5’,5’-tetramethyl[1’,3’,2’]dioxaborolan-2’-yl)-10,20-diphenylporphinato]zinc(II) (66 mg, 0.10 mmol), Ba(OH)₂•8H₂O (32 mg, 0.10 mmol), distilled H₂O (0.5 mL), and dimethoxyethane (DME) (5 mL). This mixture was degassed via three freeze-pump-thaw cycles, following which Pd(PPh₃)₄ (4 mg, 0.004 mmol) was added. After heating at 80 °C for 12 h, the mixture was partitioned
between CHCl₃ and H₂O; the organic layer was washed with H₂O (3 x 20 mL) and chromatographed on silica using an eluant polarity that increased gradually from 9:1 hexanes:THF to 7:3 hexanes:THF over the course of the separation. The third band contained the product which required further chromatography on silica (CHCl₃) to remove a closely eluting porphyrinic impurity; isolated yield = 33 mg (48% based on 42 mg of compound 9b). *anti: syn* 1:8:1 ¹H NMR (500 MHz, CDCl₃, see Figure 2 for proton labeling schematic): δ 10.24 (s'', 1 H, Hₘeso), 10.23 (s', 1 H, Hₘeso), 9.45 (d', 1 H, J=4.5 Hz, Hₜₚ), 9.42 (d'', 1 H, J=4.5 Hz, Hₜₚ), 9.38 (d', 1 H, J=4.5 Hz, H₤ₚ), 9.33 (d'', 1 H, J=4.4 Hz, H₤ₚ), 9.12 (d', 1 H, J=4.5 Hz, H₤ₚ), 9.06 (d'', 1 H, J=4.5 Hz, H₤ₚ), 9.01 (d'', 1 H, J=4.4 Hz, H₤ₚ), 8.96 (d', 1 H, J=4.4 Hz, H₤ₚ), 8.81 (d'', 1 H, J=4.6 Hz, H₤ₚ), 8.77 (d', 1 H, J=4.6 Hz, H₤ₚ), 8.73 (d', 1 H, J=4.6 Hz, H₤ₚ), 8.71 (d', 1 H, J=4.6 Hz, H₤ₚ), 8.66 (d'', 1 H, J=4.8 Hz, H₤ₚ), 8.65 (d'', 1 H, J=5.5 Hz, H₤ₚ), 8.61 (d'', 1 H, J=4.6 Hz, H₤ₚ), 8.53 (d', 1 H, J=4.5 Hz, H₤ₚ), 8.37 (d, 1 H, J=8.3 Hz, Hₐ₁₁), 8.28 (d, 1 H, J=6.8 Hz, Hₐ₁₄), 8.22-8.07 (m, 4 H, H₁₃ + Hortho,10,20 phenyls x 2), 8.02 (d(br), 1 H, J=7.4 Hz, Hortho,10,20 phenyls), 7.82 (t, 1 H, J=7.6 Hz, H₁₂), 7.77-7.59 (m, 7 H, H₁₅ + Hmeta/para,10,20 phenyls), 7.30-7.27 (m, 1 H, H₇), 6.99-6.95 (m, 2 H, H₉), 6.93 (d', 1 H, J=8.3 Hz, H₇), 6.85 (d'', 1 H, J=5.7 Hz, H₁₉), 6.76 (d', 1 H, J=5.7 Hz, H₁₆), 6.61 (d'', 1 H, J=5.8 Hz, H₁₀), 6.55 (d', 1 H, J=5.7 Hz, H₁₀), 6.25-6.22 (m, 1 H, H₁₇), 5.87 (d'', 1 H, J=8.8 Hz, H₁₈), 5.85 (d', 1 H, J=8.8 Hz, H₁₈), 5.69 (d', 1 H, J=3.1 Hz, H₁₉), 5.50 (d'', 1 H, J=3.1 Hz, H₁₉), 5.03 (t'', 1 H, J=7.6 Hz, H₈), 5.01 (t', 1 H, J=7.6 Hz, H₈), 4.91 (s'', 1 H, H₆'-xylene), 4.71 (s', 1 H, H₆'-xylene), 4.30 (s', 1 H, H₃'-xylene), 4.06 (s'', 1 H, H₃'-xylene), 3.30 (s', 3 H, OMe), 3.27 (s'', 3 H, OMe), 2.89 (s', 3 H, OMe), 2.87 (s'', 3 H, OMe), 1.02 (s', 3 H, Me), 0.91 (s'', 3 H, Me), 0.77 (d'', 1 H, J=6.9 Hz, H₇), 0.72 (d', 1 H, J=5.7 Hz, H₇), -0.88 (s'', 3 H, Me), -1.12 (s', 3 H, Me).
Vis (CH₂Cl₂): 423.8 (5.52), 548.5 (4.26). HRMS (ESI+) m/z: 1039.2948 (calcd for C₆₆H₄₈N₄O₂NaZn (M+Na) 1039.2966).

[5-(8′-[2′′,5′′-difluoro-4′′-(8′′-[2′′′, 5′′′-dimethoxyphenyl]-1′′′-naphthyl)-1′′-phenyl]-1′′-naphthyl)-10,20-diphenylporphinato]zinc(II) (10c). A 50 mL Schlenk tube was charged with 9c (15 mg, 0.024 mmol), [5-(4′,4′,5′,5′-tetramethyl[1′,3′,2′]dioxaborolan-2′-yl]-10,20-diphenylporphinato]zinc(II) (23 mg, 0.035 mmol), Ba(OH)₂•8H₂O (11 mg, 0.035 mmol), distilled H₂O (0.5 mL), and dimethoxyethane (DME) (5 mL). The mixture was degassed via three freeze-pump-thaw cycles, following which Pd(PPh₃)₄ (3 mg, 0.003 mmol) was added. After heating at 80 °C for 3 h, the mixture was partitioned between CHCl₃ and H₂O; the organic layer was washed with H₂O (3 x 20 mL), and chromatographed on silica gel (3:1 hexanes:THF). A small fraction of (5,15-diphenylporphinato)zinc(II) eluted first; the second band, eluting just prior to the red product band, contained an orange porphyrinic impurity. Isolated yield = 14 mg (57% based on 15 mg of compound 9c). anti:syn 3.3:1 ¹H NMR (500 MHz, CDCl₃, see Figure 2 for proton labeling schematic): δ 10.20 (s, 1 H, Hₘₑₙₙ), 9.41 (d, 1 H, J=4.5 Hz, Hₚ), 9.32 (d, 1 H, J=4.4 Hz, Hₚ), 9.10 (d, 1 H, J=4.4 Hz, Hₚ), 8.98 (d, 1 H, J=4.4 Hz, Hₚ), 8.84-8.81 (m, 2 H, Hₚ x 2), 8.74 (d′, 1 H, J=4.6 Hz, Hₚ), 8.72 (d′′, 1 H, J=4.6 Hz, Hₚ), 8.58 (d′, 1 H, J=4.6 Hz, Hₚ), 8.40 (d′, 1 H, J=4.6 Hz, Hₚ), 8.36 (d, 1 H, J=8.3 Hz, H₁₁), 8.27 (d, 1 H, J=8.4 Hz, H₁₄/₁₃), 8.24 (d, 1 H, J=6.8 Hz, H₁₄/₁₃), 8.22-8.13 (m, 3 H, H₂₂/₁₀₂₀ phenyls x 3), 8.04 (d′ (br), 1 H, J=7.4 Hz, Hₚ ortho, 10.20 phenyls), 8.01 (d′ (br), 1 H, J=7.5 Hz, Hₚ ortho, 10.20 phenyls), 7.82 (t, 1 H, J=7.6 Hz, H₁₂), 7.75-7.62 (m, 7 H, H₁₅ + Hₘₑₙₙ, 10.20 phenyls), 7.24 (d, 1
H, J=8.3 Hz, H₈), 7.00-6.90 (m, 3 H, H₃+H₇+H₁₅), 6.67 (d'', 1 H, J=5.6 Hz, H₁₀), 6.62 (d', 1 H, J=6.9 Hz, H₁₀), 6.32 (dd, 1 H, J=3.1 Hz, J=8.8 Hz, H₁₇), 5.90 (d'', 1 H, J=8.2 Hz, H₁₈), 5.88 (d', 1 H, J=8.8 Hz, H₁₉), 5.75-5.74 (m', 1 H, H₁₉), 5.67 (d'', 1 H, J=3.1 Hz, H₁₉), 4.94-4.85 (m, 2 H, H₆+H₆'-difluorophenyl), 3.90 (m, 1 H, H₃'-difluorophenyl), 3.32 (s', 3 H, OMe), 3.26 (s'', 3 H, OMe), 2.87 (s', 3H, OMe), 2.86 (s'', 3 H, OMe), 0.88 (d'', 1 H, J=6.6 Hz, H₃), 0.71 (d', 1 H, J=5.8 Hz, H₃). ¹⁹F NMR (200 MHz, CDCl₃): δ -119.73 (m', 1 F), -120.66 (m'', 1 F), -123.16 (m', 1 F), -125.52 (m'', 1 F). Vis (CH₂Cl₂): 420 (5.56), 508 (sh), 546 (4.17), 582 (sh). HRMS (ESI+) m/z: 1047.2491 (calcd for C₆₆H₄₂F₂N₄O₂NaZn (M+Na) 1047.2465).

Supplementary Figure Captions:

**Figure S1.** 500 MHz ¹H NMR spectrum of compound 1 in CDCl₃.

**Figure S2.** 500 MHz ¹H NMR spectra of compounds (A) 2a, (B) 2b, and (C) 2c in CDCl₃.

**Figure S3.** 500 MHz ¹H NMR spectrum of compound 5 in CDCl₃.

**Figure S4.** 500 MHz ¹H NMR spectra of compounds (A) 10a, (B) 10b, and (C) 10c in CDCl₃.
\[ ^1H \text{NMR } \text{CompD Z} \]

Solvent: CDCl₃
\[ \text{Solvent: CDCl}_3 \]

\[ \text{H NMR (CDCl}_3, \text{Z}c \text{Cmpd)} \]
'H NMR Compound 10
Solvent: CDCl₃