Supporting Information

3,3′- and 4,4′-Biphenylene Bridged Subporphyrin Dimers

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1. Experimental procedure

General

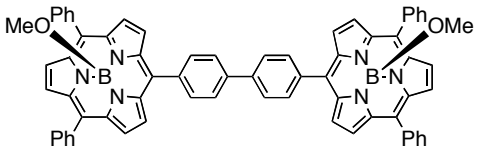
All reagents and solvents were of commercial reagent grade and were used without further purification. ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on a JEOL delta-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to internal standards ($CHCl_3$ (δ = 7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C), and an external standard, $BF_3{\cdot}OEt_2$ in $CDCl_3$ (δ = 0.00 ppm for ^{11}B)). Spectroscopic grade solvents were used for all spectroscopic studies without further purification. UV/visible absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Fluorescence spectra were recorded on a Hamamatsu Photonics C9920-02 spectrometer, and absolute fluorescence quantum yields were measured by photon-counting method using an integration sphere. ESI-TOF-MS spectra were recorded on a BRUKER DALTONICS microTOF LC using positive-ion mode. Thin layer chromatography (TLC) was performed on a silica gel sheet, MERCK silica gel 60 F_{254}. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-300) or size exclusion gel permeation chromatography (GPC) (Bio-Rad Bio-Beads S-X1, packed with THF).

Pyridine–tri-*N*-pyrrolylborane was prepared by the reported procedure.[S1] Dry *N*,*N*-dimethylformamide was distilled from CaH_2.

4,4′-Biphenylene bridged dimer 1

To a suspension of pyridine–tri-*N*-pyrrolylborane (1.50 g, 5.21 mmol) in 1,2-dichlorobenzene 225 ml, were added benzaldehyde (1.12 ml, 11.00 mmol) and 4-bromobenzaldehyde (0.83 g, 4.50 mmol), and the mixture was cooled to 0 °C with an ice/water bath. After dropwise addition of trifluoroacetic acid (0.50 ml, 6.73 mmol) *via* syringe, the solution was stirred for 1 h at 0 °C under N_2. The acid was quenched with 0.60 ml of pyridine, and the resulting solution was refluxed for 1 h under aerobic conditions. After the solution was cooled to room temperature, the solvent was removed in vacuo. To the residual black tar, a mixture of THF/MeOH (1:1) 50 ml was added and heated at 50 °C for 10 min. After the removal of insoluble materials by filtration, the solvent was once evaporated, and the residue was mounted onto a GPC column (6 × 40 cm, packed with THF) with a minimal amount of THF. Polymeric byproducts that eluted first was removed and the yellowish fractions that eluted around R_f = 0.50 on TLC (silica gel; eluent: CH_2Cl_2/hexane/ether=1:2:1) were collected. After passing through a short silica gel column (eluent: CH_2Cl_2/hexane/ether=1:1:1), the crude mixture was dissolved in 30 ml of CH_2Cl_2 and treated with 10 g of MnO_2 at room temperature overnight with vigorous stirring. The oxidant was removed by passing the suspension through a short Celite® pad. Further purification by silica gel column chromatography (eluent: CH_2Cl_2/hexane/ether=1:2:1) gave a crude mixture of subporphyrins as orange-brown solid.

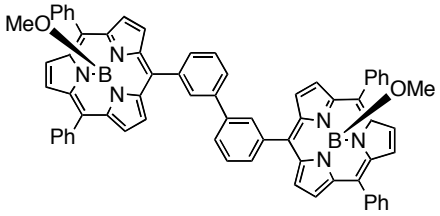
A 50 ml Schlenk tube was charged with the subporphyrin mixture, dry DMF (5 ml) $NiCl_2$(diphenylphosphinopropane) (25 mg, 46 μmol), zinc powder (100 mg), and potassium iodide (100 mg). The resulting solution was deoxygenated *via* three freeze-pump-thaw cycles, and then stirred at 80 °C for 12 h under N_2 atmosphere. The resulting mixture was filtered, the filtrate was poured into 50 ml of water, and the products were extracted with CH_2Cl_2 (20 ml × 3). Combined organic layer was washed with brine and water, dried over Na_2SO_4, and the solvent was evaporated. The products were separated by GPC column (4 × 90 cm) to give dimer **1** as the second-to-last fraction and triphenylsubporphyrin **3** as the last fraction. Recrystallization from CH_2Cl_2/MeOH afforded **1** (30 mg, 1.3%) and **3** (62 mg, 2.4%) as orange crystalline solids.



^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.27 (d, J = 8.2 Hz, 4H, biphenylene bridge), 8.26 (d, J = 4.6 Hz, 4H, β-H), 8.18 (d, J = 4.6 Hz, 4H, β-H), 8.15 (d, J = 8.2 Hz, 4H, biphenylene bridge), 8.15 (s, 4H, β-H), 8.10 (d, J = 7.4 Hz, 8H, *meso*-Ph-*o*-H), 7.72 (t, J = 7.8 Hz, 8H, *meso*-Ph-*m*-H), 7.63 (t, J = 7.3 Hz, 4H, *meso*-Ph-*p*-H), and 0.89 (s, 6H, axial-OMe); ^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) –15.2 (s, 2B); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 141.2, 141.1, 140.5, 140.1, 137.3, 136.8, 133.9, 133.3, 128.8, 128.0, 127.6, 122.6, 122.5, 122.4, 122.3, 120.8 and 46.9 (axial-OCH_3); HR-ESI TOF-MS (positive mode) m/z = 969.3696 (calcd. for $C_{67}O_1H_{43}N_6B_2$ = 969.3699 [M–OMe]$^+$); UV-vis (in CH_2Cl_2) λ [nm](ε [$M^{-1}cm^{-1}$]) 379(263000), 463(29000), and 494(32000); Fluorescence (in CH_2Cl_2, λ_{ex} = 379 nm); λ_{max} [nm] = 531, Φ_F = 0.28.

3,3′-Biphenylene bridged dimer 2

3,3′-dimer was synthesized from pyridine–tri-*N*-pyrrolylborane (1.50 g, 5.21 mmol), benzaldehyde (1.12 ml, 11.00 mmol) and 3-bromobenzaldehyde (0.52 ml, 4.50 mmol) according to the same procedure as **1** in 1.0% yield (20 mg) along with triphenylsubporphyin **3** (60 mg, 2.3%).

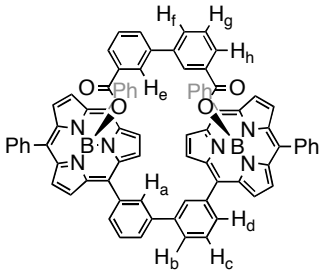


^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.49 (s, 2H, biphenylene bridge), 8.21 (d, J = 4.6 Hz, 4H, β-H), 8.13 (d, J = 4.6 Hz, 4H, β-H), 8.12 (s, 4H, β-H), 8.10 (d, J = 7.8 Hz, 2H, biphenylene bridge), 8.06 (d, J = 7.3 Hz, 8H, *meso*-Ph-*o*-H), 8.03 (d, J = 7.8 Hz, 2H, biphenylene bridge), 7.84 (t, J = 7.8 Hz, 2H, biphenylene bridge), 7.69 (t, J = 7.8 Hz, 8H, *meso*-Ph-*m*-H), 7.61 (t, J = 7.3 Hz, 4H, *meso*-Ph-*p*-H), and 0.85 (s, 6H, axial-OMe); ^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) –15.2 (s, 2B); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 141.4, 141.2, 141.1, 138.2, 137.7, 133.4, 132.6, 132.3, 129.4, 128.8,

127.9, 126.9, 122.5, 122.4 (2C), 120.8, 120.3, 119.9, and 47.0 (axial-OCH_3); HR-ESI TOF-MS (positive mode) m/z = 969.3694, 1023.3789 (calcd. for $C_{67}O_1H_{43}N_6B_2$ = 969.3699 [M–OMe]$^+$, $C_{68}O_2H_{46}N_6B_2Na$ = 1023.3781 [M+Na]$^+$); UV-vis (in CH_2Cl_2) λ [nm](ε [$M^{-1}cm^{-1}$]) 374(310000), 461(27000), and 486(21000); Fluorescence (in CH_2Cl_2, λ_{ex} = 374 nm); λ_{max} [nm] = 516, Φ_F = 0.15.

Cyclic dimer 5

Dimer **2** (4.8 mg, 5.0 μmol) and biphenyl-3,3′-dicarboxylic acid (**4**) (1.2 mg, 5.0 μmol) were dissolved in toluene 40 ml and refluxed with a Dean-Stark trap for 6 h. Evaporation of the solvent gave orange crystalline solid of **5** quantitatively.



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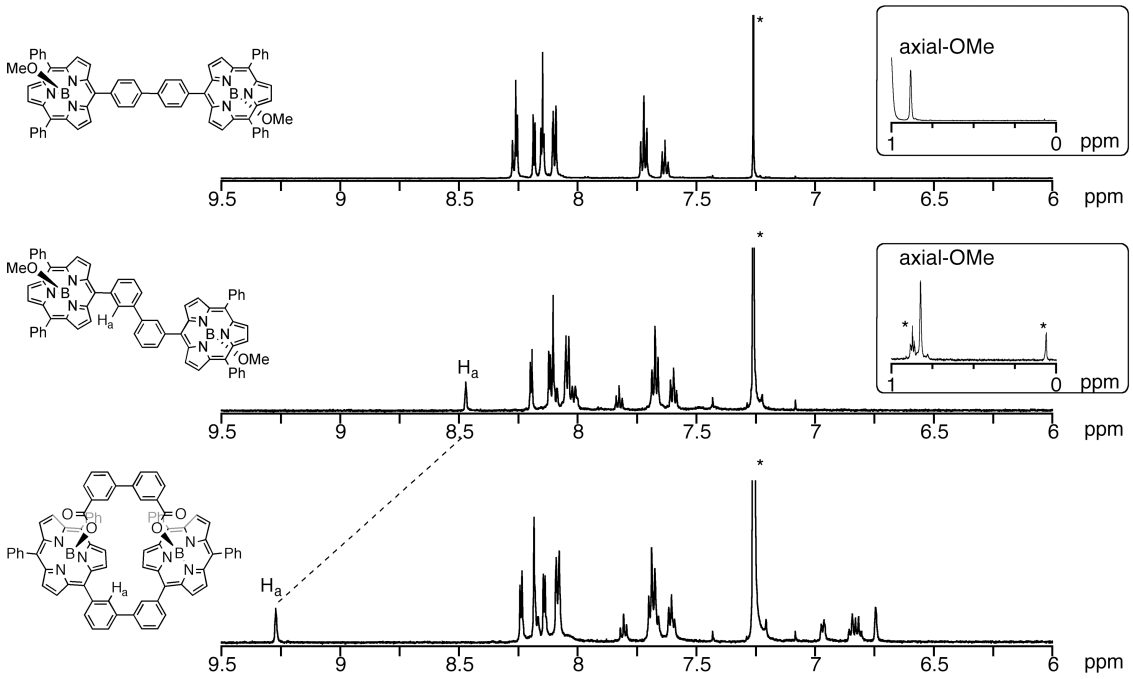
This material was stable in the solid state, however, it was partially hydrolyzed by adventitious water to release axial ligand after overnight storing in solution.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.27 (s, 2H, biphenylene H_a), 8.24 (d, J = 4.6 Hz, 4H, β-H), 8.18 (s and d, 4 + 2H, β-H and biphenylene H_d), 8.14 (d, J = 4.6 Hz, 4H, β-H), 8.08 (d, J = 6.9 Hz, 8H, *meso*-Ph-*o*-H), 7.81 (t, J = 7.8 Hz, 2H, biphenylene H_c), 7.70–7.65 (t and d, 8 + 2H, *meso*-Ph-*m*-H and biphenylene H_b), 7.60 (t, J = 7.3 Hz, 4H, *meso*-Ph-*p*-H), 6.97 (d, J = 7.4 Hz, 2H, axial ligand H_f), 6.85 (d, J = 7.8 Hz, 2H, axial ligand H_h), 6.82 (t, J = 7.8 Hz, 2H, axial ligand H_g), and 6.75 (s, 2H, axial ligand H_e); ^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) –15.2 (br s, 2B); HR-ESI TOF-MS (positive mode) m/z = 1179.4028 (calcd. for $C_{80}O_4H_{49}N_6B_2$ = 1179.4019 [M]$^+$); UV-vis (in CH_2Cl_2) λ [nm](ε [$M^{-1}cm^{-1}$]) 371(297000), 458(27000), and 481(17000); Fluorescence (in CH_2Cl_2, λ_{ex} = 374 nm); λ_{max} [nm] = 516, Φ_F = 0.16.

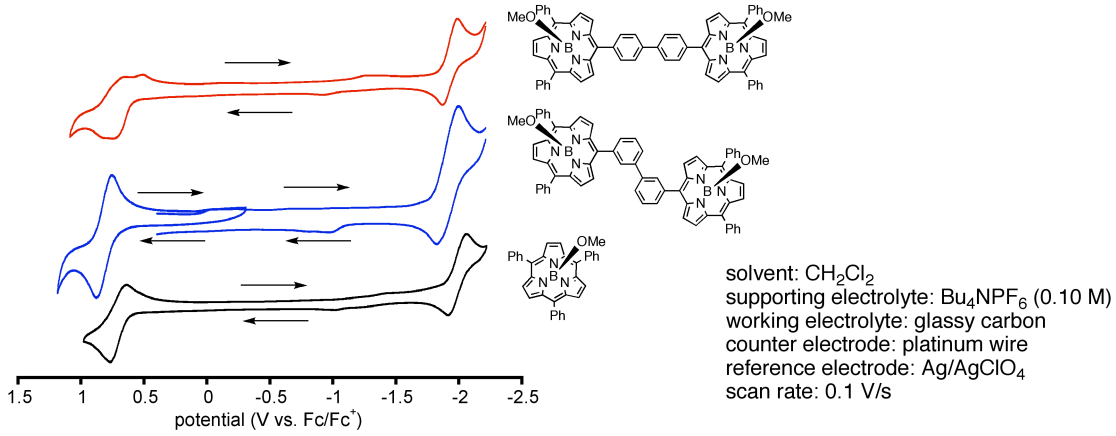
2. ^{1}H NMR spectra

Figure S1. ^{1}H NMR spectra of **1**, **2**, and **5** in $CDCl_3$.



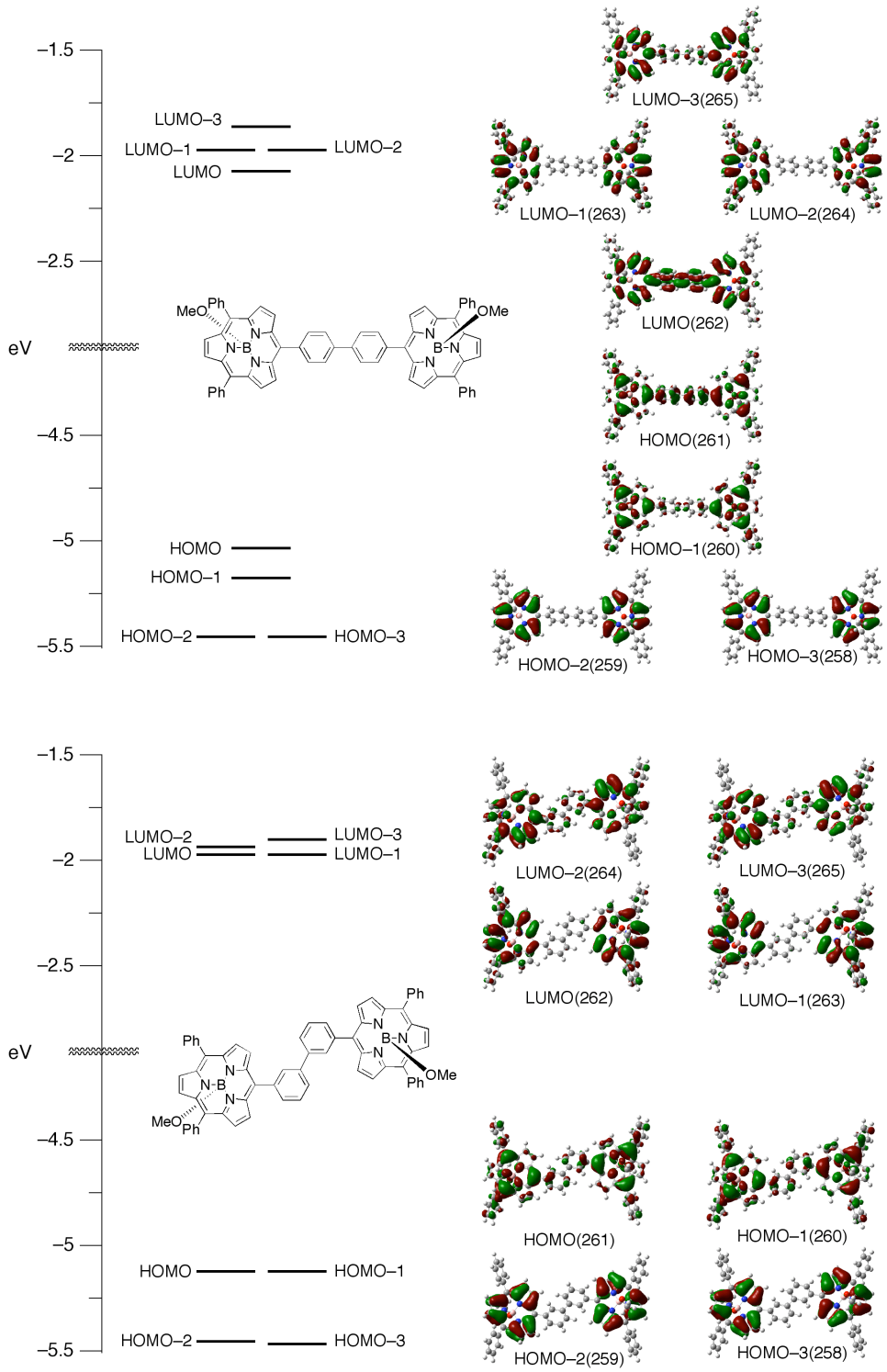
3. Cyclic voltammetry

Figure S2. Cyclic voltammograms of **1**, **2**, and **3** in CH_2Cl_2 containing 0.10 M Bu_4NPF_6.



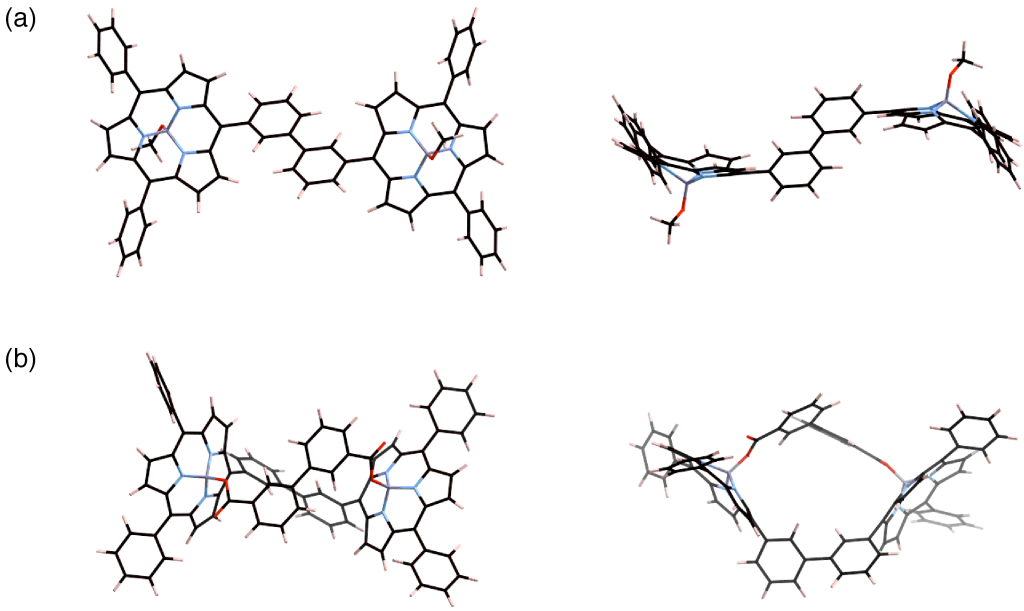
4. MO diagram

Figure S3. MO diagrams of **1** and **2** calculated at the B3LYP/6-31G* level.[S2]



5. Optimized structures

Figure S4. Optimized structures of (a) **2** and (b) **5** at the B3LYP/6-31G* level.



6. References

1. P. Szarvas, B. Györi and J. Emri *Acta. Chim. (Budapest)*, 1971, **70**, 1.
2. Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.