Supplementary Information

Complementary face-to-face dimer formation from *meso*-aryl subporphyrins bearing a 2-carboxyphenyl group

Yasuhide Inokuma and Atsuhiro Osuka*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

Contents

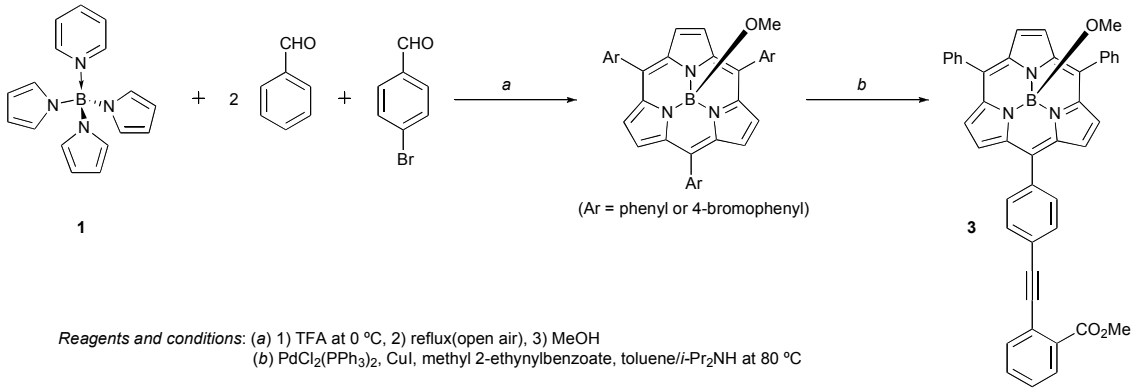
1. Experimental procedure

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 Shimadzu RF-5300PC spectrometer with spectroscopic grade solvents. Relative fluorescence quantum yields were determined with a reference to that of 8-amino-1-naphthalenesulfonic acid (Φ_f = 0.37 in ethanol). ESI-TOF-MS spectra were recorded on a BRUKER DALTONICS micro TOF 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 in a 6 × 40 cm gravity column).

Pyridine–tri-*N*-pyrrolylborane (**1**)[1] and methoxo(5,10,15-tri(4-bromophenyl)subporphyrinato)-boron(III) (**5**)[2] were prepared by the reported procedure.[1] Dry toluene was purchased from Wako (Toluene, Dehydrated) and was used as received. Dry diisopropylamine was distilled from CaH_2.

Scheme S1.

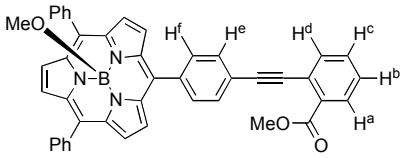


Reagents and conditions: (*a*) 1) TFA at 0 ºC, 2) reflux(open air), 3) MeOH
(*b*) $PdCl_2(PPh_3)_2$, CuI, methyl 2-ethynylbenzoate, toluene/*i*-Pr_2NH at 80 ºC

Methoxo(5,10-diphenyl-15-(4-(2-methoxycarbonylphenylethynyl)phenyl)subporphyrinato)boron(III) (**3**)

To a suspension of pyridine–tri-*N*-pyrrolylborane (**1**) (3.00 g, 10.4 mmol) in 1,2-dichlorobenzene 400 ml, were added benzaldehyde (2.12 ml, 20.8 mmol) and 4-bromobenzaldehyde (1.93 g, 10.4 mmol), and the mixture was cooled to 0 ºC with an ice/water bath. After dropwise addition of trifluoroacetic acid (1.07 ml, 14.4 mmol) *via* syringe, the solution was stirred for 1 h at 0 ºC under N_2. The acid was quenched with 0.90 ml of pyridine, and then 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 ºC for 10 min. After the removal of insoluble materials by filtration, the solvent was once evaporated, then the residue was mounted onto a GPC column (8 × 50 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. 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 toluene (12 ml) and diisopropylamine (3 ml), copper(I) iodide (5 mg, 26.3 μmol), dichlorobis(triphenylphosphine)palladium(II) (15 mg, 21.4 μmol), and excess methyl 2-ethynylbenzoate (ca. 0.2 ml). The resulting solution was deoxygenated *via* three freeze-pump-thaw cycles, and then stirred at 80 ºC for 12 h under Ar atmosphere. After passing through a short Celite® column(2×4 cm), the solvent was evaporated to dryness. The residual solid was once dissolved in a mixture of CH_2Cl_2/MeOH (1:1, 20 ml) and then the solvent was evaporated again. The residue was chromatographed on silica gel (eluent: CH_2Cl_2/hexane/ether=1:2:1) to give triphenylsubporphyrin as the first fraction (R_f=0.54), and

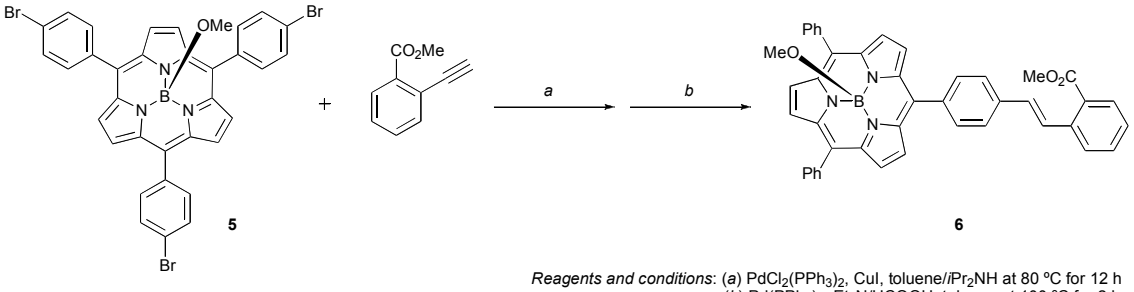
the target subporphyrin **3** as the second fraction (R_f=0.35). Recrystallization from CH_2Cl_2/MeOH yielded triphenylsubporphyrin (79 mg, 1.5%) and subporphyrin **3** (85 mg, 1.2%), both as orange crystalline solids.



3

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.15 (d, *J* = 4.6 Hz, 2H, *β*-H), 8.14 (d, *J* = 4.6 Hz, 2H, *β*-H), 8.13 (s, 2H, *β*-H), 8.09 (d, *J* = 8.2 Hz, 2H, phenylene-H^f), 8.07 (d, *J* = 8.3 Hz, 4H, Ph-*o*-H), 8.04 (d, *J* = 7.9 Hz, 1H, H^a), 7.91 (d, *J* = 8.2 Hz, 2H, phenylene-H^e), 7.75 (d, *J* = 7.7 Hz, 1H, H^d), 7.71 (t, *J* = 7.8 Hz, 4H, Ph-*m*-H), 7.62 (t, *J* = 7.6 Hz, 2H, Ph-*p*-H), 7.56 (t, *J* = 7.6 Hz, 1H, H^c), 7.44 (t, *J* = 7.8 Hz, 1H, H^b), 4.04 (s, 3H, COOMe), and 0.85 (s, 3H, axial-OMe); ^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) –15.2 (s, 1B); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 166.8 (carbonyl), 141.3, 141.1 (2C), 137.7, 137.3, 134.2, 133.4, 133.3, 132.1(2C), 131.9, 130.7, 128.8, 128.2, 128.0, 123.9, 123.0, 122.6, 122.5, 122.2, 120.9, 119.7, 94.3 (acetylene), 89.9 (acetylene), 52.4 (ester-OCH_3), and 47.0 (axial-OCH_3); HR-ESI TOF-MS (positive mode) *m*/*z* = 628.2193 (calcd. for $C_{43}O_2H_{27}N_3B_1$ = 628.2198 [*M*–OMe]$^+$); UV-vis (in CH_2Cl_2) λ [nm](ε [$M^{-1}cm^{-1}$]) 379(154000), 464(13000), and 491(13000); Fluorescence (in CH_2Cl_2, λ_{ex} = 379 nm); λ_{max} [nm] = 530, Φ_F = 0.20.

Scheme S2.

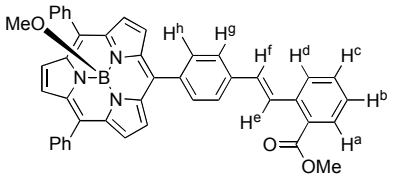


Reagents and conditions: (*a*) $PdCl_2(PPh_3)_2$, CuI, toluene/*i*Pr_2NH at 80 ºC for 12 h
(*b*) $Pd(PPh_3)_4$, Et_3N/HCOOH, toluene at 100 ºC for 2 h

Methoxo(5,10-diphenyl-15-(4-(*trans*-2-methoxycarbonylstyryl)phenyl)subporphyrinato)boron(III) (6)

A 50 ml Schlenk flask was charged with methoxo(5,10,15-tri(4-bromophenyl)-subporphyrinato)boron(III) (**5**) (100 mg, 135 μmol), copper(I) iodide (1.4 mg, 7.1 μmol), dichlorobis(triphenylphosphine)palladium(II) (5 mg, 7.1 μmol), dry toluene (6 ml), dry diisopropylamine (5 ml), and methyl 2-ethynylbenzoate (30.4 mg, 190 μmol). The mixture was

degassed *via* three freeze-pump-thaw cycles. The resulting solution was stirred at 80 °C under Ar for 12 h. After cooling of the reaction mixture to room temperature, it was passed through a short Celite® column, and the solvent was evaporated. Residual solid was placed again in a 50 ml Schlenk flask. Tetrakis(triphenylphosphine)palladium(0) (50 mg, 43.3 μmol), dry toluene (13 ml), triethylamine (0.25 ml), and formic acid (0.25 ml) were added to the flask under nitrogen atmosphere, and the mixture was stirred at 100 °C for 2 h under inert atmosphere. After cooling to room temperature, the resulting solution was diluted with CH_2Cl_2 (ca. 30 ml), washed with sat. $NaHCO_3$ aq. (50 ml × 3 times), and dried over anhydrous Na_2SO_4. After the evaporation of the solvent to dryness, the axial ligand of subporphyrins was fixed as methoxo-form by heating in a mixture of CH_2Cl_2/MeOH (1:1) at 50 °C for 10 min. The mixture was chromatographed on silica gel (eluent: CH_2Cl_2/hexane/ether=1:2:1) to give triphenylsubporphyrin as the first fraction (R_f=0.54), and the target subporphyrin **5** as the second fraction (R_f=0.37). Recrystallization from CH_2Cl_2/MeOH yielded triphenylsubporphyrin (6 mg, 8.9%) and subporphyrin **6** (21 mg, 24%) as both orange crystalline solids.



6

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.22 (d, *J* = 16.1 Hz, 1H, vinyl-H^e), 8.16 (d, *J* = 4.6 Hz, 2H, *β*-H), 8.14 (d, *J* = 4.6 Hz, 2H, *β*-H) 8.12 (s, 2H, *β*-H), 8.09-8.06 (m, 6H, Ph-*o*-H and phenylene-H^h), 8.00 (d, *J* = 7.8 Hz, 1H, H^a), 7.88 (d, *J* = 7.8 Hz, 2H, phenylene-H^g), 7.83 (d, *J* = 8.2 Hz, 1H, H^d), 7.70 (t, *J* = 7.8 Hz, 4H, Ph-*m*-H), 7.62 (t, *J* = 7.8 Hz, 2H, Ph-*p*-H), 7.59 (t, *J* = 7.5 Hz, 1H, H^c), 7.38 (t, *J* = 7.8 Hz, 1H, H^b), 7.21 (d, *J* = 16.1 Hz, 1H, vinyl-H^f), 3.98 (s, 3H, COOMe), and 0.85 (s, 3H, axial-OMe)); ^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) –15.2 (s, 1B); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 168.0 (carbonyl), 141.2, 141.0 (2C), 139.4, 137.4, 137.1, 136.9, 133.7, 133.4, 132.4 (*C*-H^c), 131.0 (2C, vinyl *C*-H^f and aryl-*C*-H^a), 128.8 (2C), 128.5 (vinyl *C*-H^e), 127.9, 127.5 (*C*-H^b), 127.3 (2C), 122.4 (3C), 120.7, 120.3, 52.4 (ester-OCH_3), and 47.0 (axial-OCH_3); HR-ESI TOF-MS (positive mode) *m*/*z* = 630.2350 (calcd. for $C_{43}O_2H_{29}N_3B_1$ = 630.2355 [*M*–OMe]$^+$); UV-vis (in CH_2Cl_2) λ [nm](ε [$M^{-1}cm^{-1}$]) 380(151000), 464(14000), and 492(15000); Fluorescence (in CH_2Cl_2, λ_{ex} = 380 nm); λ_{max} [nm] = 535, Φ_F = 0.20.

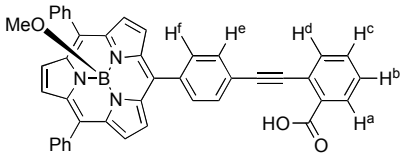
General procedure for hydrolysis of esters

Ester (**3** or **6**) was dissolved in a mixture of THF/MeOH/8 M NaOH aq. (3/2/1; ca. 2 mM for subporphyrin), and the solution was stirred at room temperature for overnight. The mixture was diluted with water (equal volume of the solution), acidified with 10% hydrochloric acid, and extracted with CH_2Cl_2. The combined organic phase was washed twice with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. Residual orange solid was dissolved in a mixture of CH_2Cl_2/MeOH (1/1), and evaporated again to dryness. Resulting solid was recrystallized from CH_2Cl_2/hexane to give pure carboxylic acid (**4** or **7**) as orange flakes.

Methoxo(5,10-diphenyl-15-(4-(2-carboxyphenylethynyl)phenyl)subporphyrinato)boron(III) (**4**)

Purification and handling of this compound require meticulous care. In an alcoholic solution, 2-tolancarboxylic acid unit undergoes isomerization by heating. Thus, evaporation of the solvent must be done at r.t. without heating the solution.

According to the general procedure, 36 mg of carboxylic acid **4** was obtained from 41 mg (62 μmol) of ester **3** in 90% yield.



4

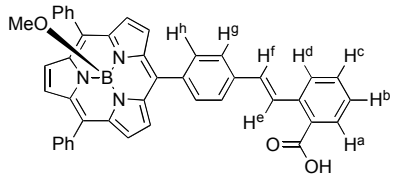
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.14 (d, J = 4.6 Hz, 2H, β-H), 8.13-8.11 (s and d, 4H, β-H), 8.10 (d, J = 7.8 Hz, 1H, H^a), 8.07 (d, J = 8.3 Hz, 2H, phenylene-H^f), 8.06 (d, J = 7.6 Hz, 4H, Ph-o-H), 7.90 (d, J = 8.3 Hz, 2H, phenylene-H^e), 7.75 (d, J = 7.6 Hz, 1H, H^d), 7.70 (t, J = 7.8 Hz, 4H, Ph-m-H), 7.61 (t, J = 7.6 Hz, 2H, Ph-p-H), 7.57 (t, J = 7.6 Hz, 1H, H^c), 7.45 (t, J = 7.8 Hz, 1H, H^b), and 0.83 (s, 3H, axial-OMe); ^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) –15.2 (s, 1B); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 168.6 (carbonyl), 141.0, 140.8 (2C), 137.3, 136.9, 134.0, 133.1, 133.0, 132.5, 131.9, 131.7, 130.7, 128.7, 128.1, 127.9, 123.6, 123.1, 122.5, 122.4, 122.1, 120.9, 119.7, 94.0 (acetylene), 89.9 (acetylene), and 46.4 (axial-OCH_3); HR-ESI TOF-MS (positive mode) m/z = 614.2045 (calcd. for $C_{42}O_2H_{25}N_3B_1$ = 614.2041 [M–OMe]$^+$); UV-vis (in CH_2Cl_2) λ [nm](ε [$M^{-1}cm^{-1}$]) 379(163000), 463(14000), and 491(15000); Fluorescence (in CH_2Cl_2, λ_{ex} = 379 nm); λ_{max} [nm] = 528,

Φ_F = 0.17.

Proton peak of –COOH was not observed due to weak and broadened signal.

Methoxo(5,10-diphenyl-15-(4-(*trans*-2-carboxystyryl)phenyl)subporphyrinato)boron(III) (**7**)

According to the general procedure, 18 mg of carboxylic acid **7** was obtained from 20 mg (30 μmol) of ester **6** in 92% yield.



7

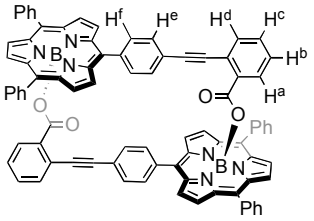
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.20 (d, *J* = 16.0 Hz, 1H, vinyl-H^e), 8.13 (d, *J* = 4.6 Hz, 2H, *β*-H), 8.10 (d, *J* = 4.6 Hz, 2H, *β*-H), 8.09 (s, 2H, *β*-H), 8.03 (d, *J* = 7.8 Hz, 2H, phenylene-H^h), 8.01 (d, *J* = 8.3 Hz, 4H, Ph-*o*-H), 7.99 (d, *J* = 7.8 Hz, 1H, H^a), 7.84 (d, *J* = 8.3 Hz, 2H, phenylene-H^g), 7.78 (d, *J* = 7.8 Hz, 1H, H^d), 7.66 (t, 7.6 Hz, 4H, Ph-*m*-H), 7.57 (t, *J* = 7.3 Hz, 2H, Ph-*p*-H), 7.52 (t, *J* = 7.1 Hz, 1H, H^c), 7.33 (t, *J* = 7.6 Hz, 1H, H^b), 7.16 (d, *J* = 16.0 Hz, 1H, vinyl-H^f), and 0.77 (s, 3H, axial-OMe); ^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) –15.2 (s, 1B); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 170.0 (carbonyl), 141.0, 140.9 (2C), 139.2, 137.2, 137.1, 136.6, 133.5, 133.2, 132.3, 131.2, 130.5, 129.2, 128.8, 128.7, 127.9, 127.4, 127.2, 127.1, 122.4 (2C), 122.3, 120.7, 120.4, and 46.6 (axial-OMe); HR-ESI TOF-MS (negative mode) *m*/*z* = 646.2300 (calcd. for $C_{43}O_3H_{29}N_3B_1$ = 646.2304 [*M*–H]$^-$); UV-vis (in CH_2Cl_2) λ [nm](ε [$M^{-1}cm^{-1}$]) 381(159000), 464(15000), and 492(16000); Fluorescence (in CH_2Cl_2, λ_{ex} = 380 nm); λ_{max} [nm] = 533, Φ_F = 0.16.

Proton peak of –COOH was not observed due to weak and broadened signal.

Dimerization of subporphyrin–carboxylic acid 4

A 200 μM toluene solution of subporphyrin **4** was refluxed for 12 h in a round-bottom flask equipped with a Dean-Stark trap under nitrogen atmosphere. Evaporation of the solvent to dryness gave subporphyrin dimer **8** quantitatively as an orange crystalline solid.

(Analytical sample was prepared by recrystallization of the product from CH_2Cl_2/hexane.)



8

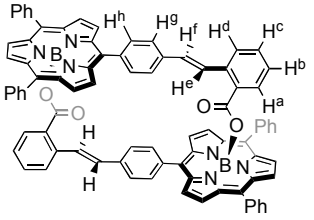
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.27 (d, *J* = 4.6 Hz, 4H, *β*-H), 8.26 (s, 4H, *β*-H), 8.23 (d, *J* = 4.6 Hz, 4H, *β*-H), 8.14 (d, *J* = 7.3 Hz, 8H, Ph-*o*-H), 8.12 (d, *J* = 7.8 Hz, 4H, phenylene-H^f), 7.73 (t, *J* = 7.6 Hz, 8H, Ph-*m*-H), 7.71 (d, *J* = 7.8 Hz, 4H, phenylene-H^e), 7.64 (t, *J* = 7.4 Hz, 4H, Ph-*p*-H), 7.18 (d, *J* = 7.3 Hz, 2H, H^d), 7.07 (t, *J* = 7.4 Hz, 2H, H^c), 6.90 (t, *J* = 7.6 Hz, 2H, H^b), and 6.84 (d, *J* = 7.8 Hz, 2H, H^a); ^{11}B NMR (193 MHz, $CDCl_3$) δ (ppm) –15.2 (br s, 1B); HR-ESI TOF-MS (positive mode) *m*/*z* = 1249.3837 (calcd. for $C_{84}O_4H_{48}N_6B_2Na_1$= 1249.3839 [*M*+Na]$^+$); UV-vis (in CH_2Cl_2) λ [nm](ε [$M^{-1}cm^{-1}$]) 379(293000), 463(27000), and 490(25000); Fluorescence (in CH_2Cl_2, λ_{ex} = 379 nm); λ_{max} [nm] = 524, Φ_F = 0.21.

^{13}C NMR spectrum could not be recorded due to the low solubility.

Dimerization of subporphyrin–carboxylic acid 7

A 100 *μ*M toluene solution of subporphyrin **7** was refluxed for 3 h in a round-bottom flask equipped with a Dean-Stark trap under nitrogen atmosphere. Evaporation of the solvent to dryness gave subporphyrin dimer **9** quantitatively as an orange crystalline solid.

(Analytical sample was prepared by recrystallization of the product from CH_2Cl_2/hexane.)



9

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.40 (d, *J* = 4.6 Hz, 4H, *β*-H), 8.30 (d, *J* = 4.6 Hz, 4H, *β*-H), 8.23 (s, 4H, *β*-H), 8.16 (d, *J* = 7.3 Hz, 8H, Ph-*o*-H), 8.01 (d, *J* = 7.8 Hz, 4H, phenylene-H^h), 7.73 (t, *J* = 7.6 Hz, 8H, Ph-*m*-H), 7.64 (t, *J* = 7.4 Hz, Ph-*p*-H), 7.60 (d, *J* = 7.8 Hz, 4H, phenylene-H^g), 7.19 (d, *J* = 8.3 Hz, 2H, H^d), 7.10 (t, *J* = 7.4 Hz, 2H, H^c), 7.00 (d, *J* = 8.2 Hz, 2H, H^a), 6.90 (t, *J* = 7.8 Hz, 2H, H^b), 6.58 (d, *J* = 16.0 Hz, 2H, vinyl-H^e or H^f), and 6.53 (d, *J* = 16.0 Hz, 2H, vinyl-H^e or H^f); ^{11}B

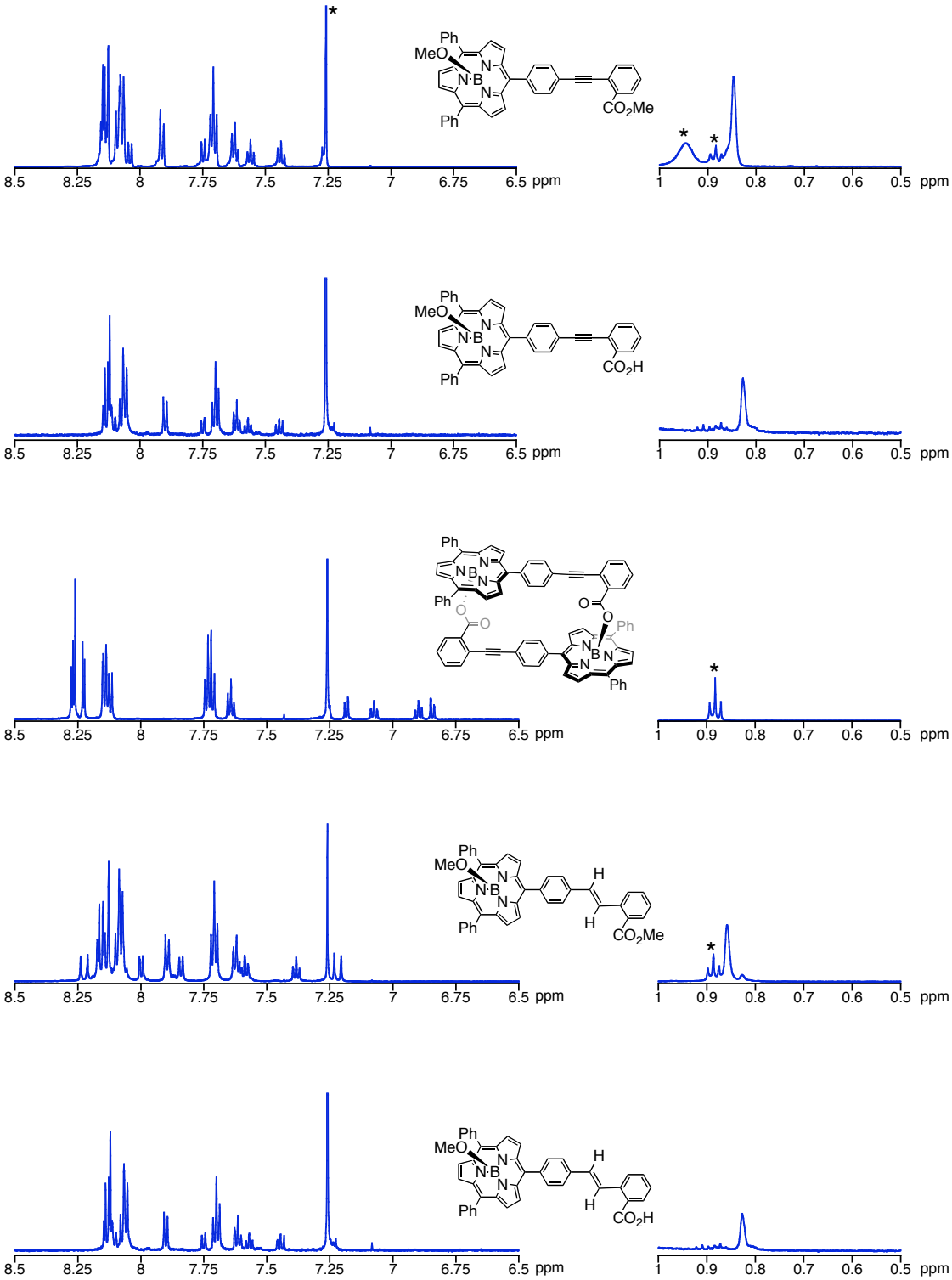
NMR (193 MHz, $CDCl_3$) δ (ppm) –15.3 (br s, 1B); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 165.9 (carbonyl), 141.5, 140.7, 140.4, 137.4, 137.2, 136.4, 133.7, 133.4 (2C), 131.5, 130.6, 130.2, 129.4, 129.3, 128.9, 128.1, 127.7, 126.8, 126.7, 122.7, 122.6 (2C), 121.9, and 121.0; HR-ESI TOF-MS (positive mode) m/z = 1253.4160 (calcd. for $C_{84}O_4H_{52}N_6B_2Na_1$= 1253.4152 $[M+Na]^+$); UV-vis (in CH_2Cl_2) λ [nm](ε $[M^{-1}cm^{-1}]$) 382(313000), 464(31000), and 493(35000); Fluorescence (in CH_2Cl_2, λ_{ex} = 383 nm); λ_{max} [nm] = 533, Φ_F = 0.20.

Methanolysis of dimer 9

Dimer **9** was dissolved in a minimal amount of CH_2Cl_2/MeOH (1:1) mixture. The solution was stirred at 40 ºC for 15 min, and then the solvent was evaporated to give monomer **7** quantitatively.

2. ^{1}H NMR spectra

Figure S1. ^{1}H NMR spectra of subporphyrins **3**, **4**, **6**, **7**, **8**, and **9** in $CDCl_3$. (*: solvent peaks)



(Figure S1. continued)

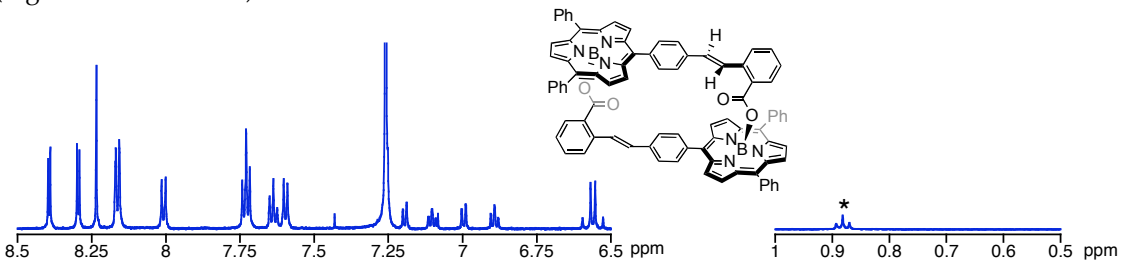
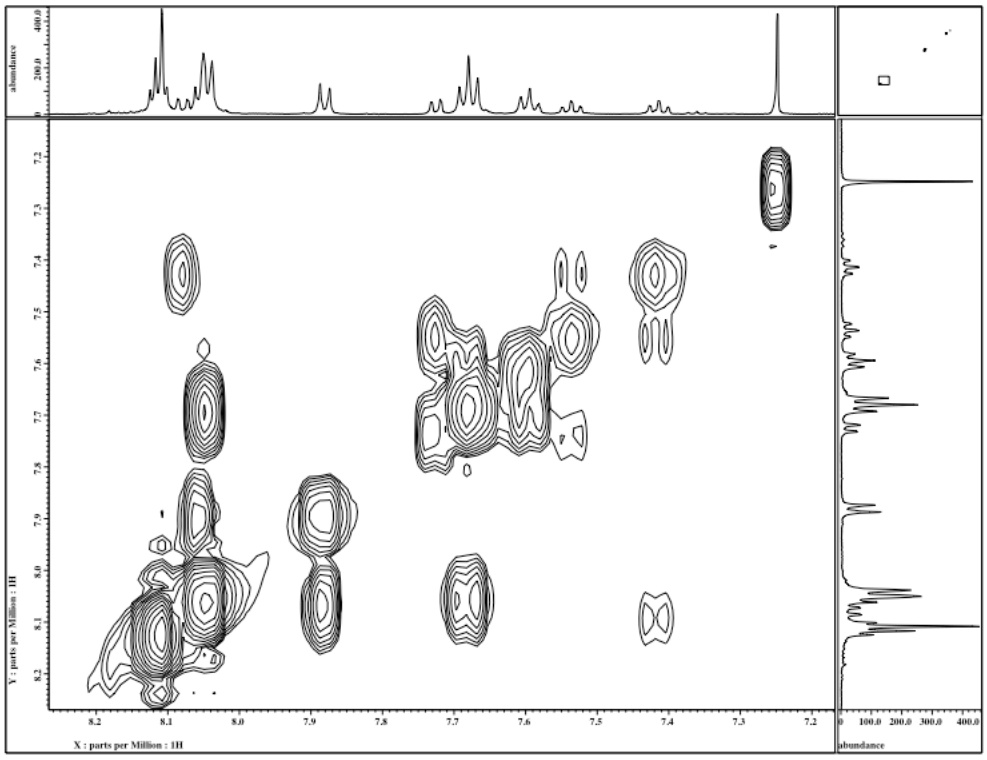


Figure S2. ^{1}H-^{1}H COSY NMR spectra of monomer **4** and dimer **8** in $CDCl_3$.



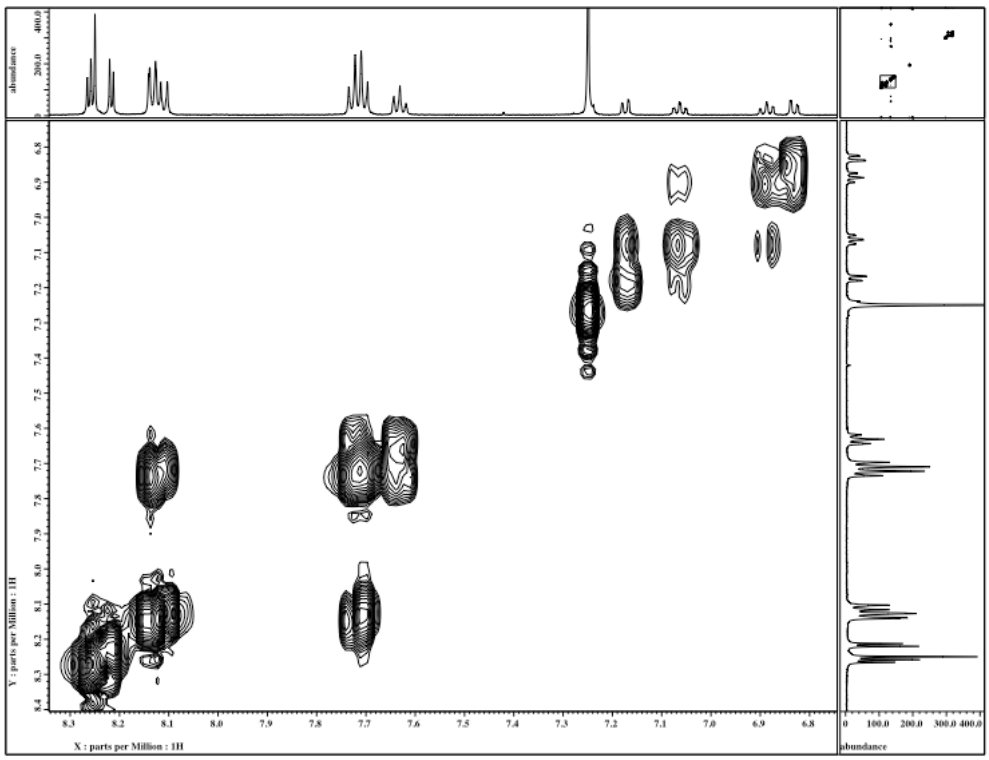


Figure S3. ^{13}C-^{1}H COSY NMR spectra of **6** in $CDCl_3$.

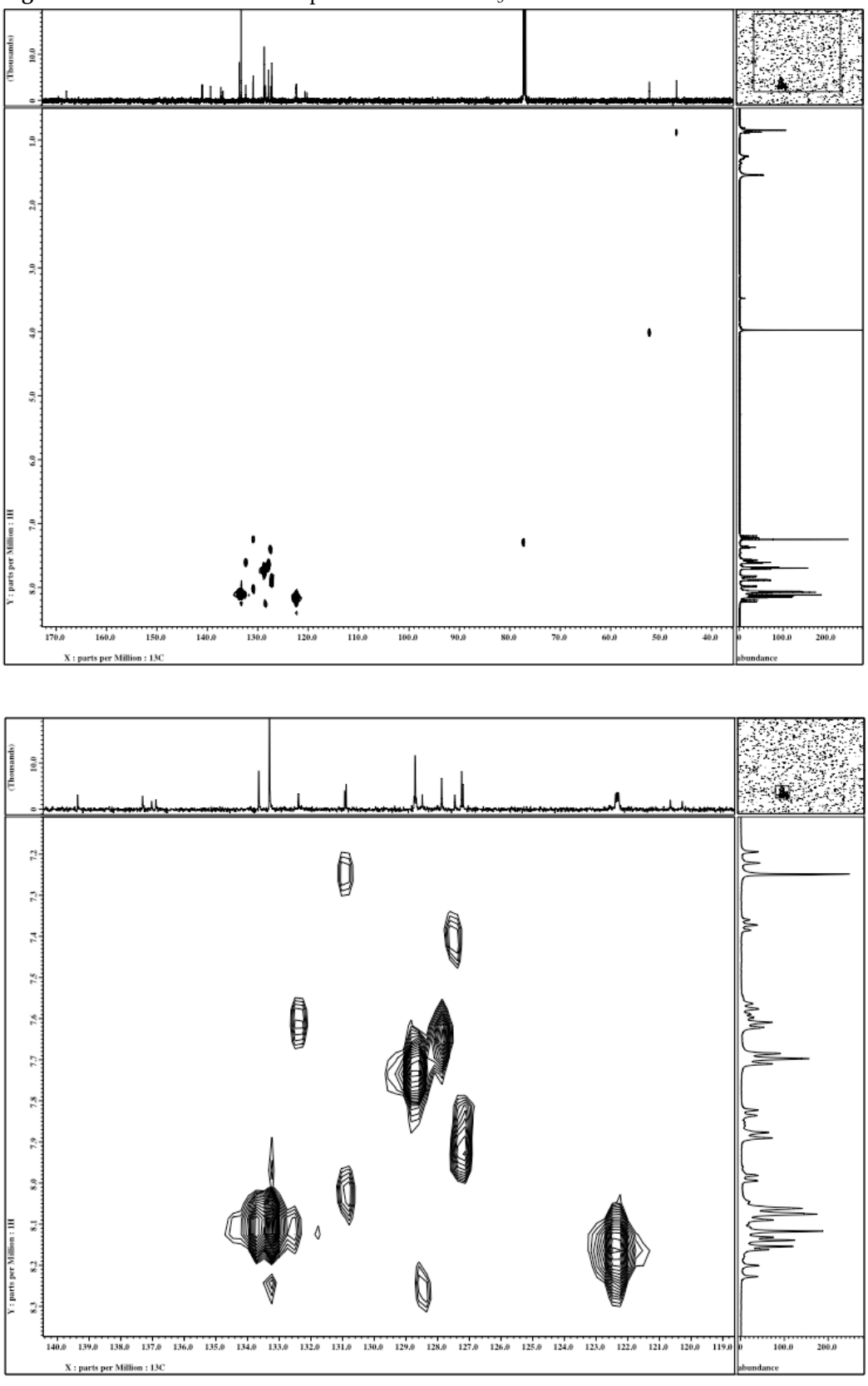
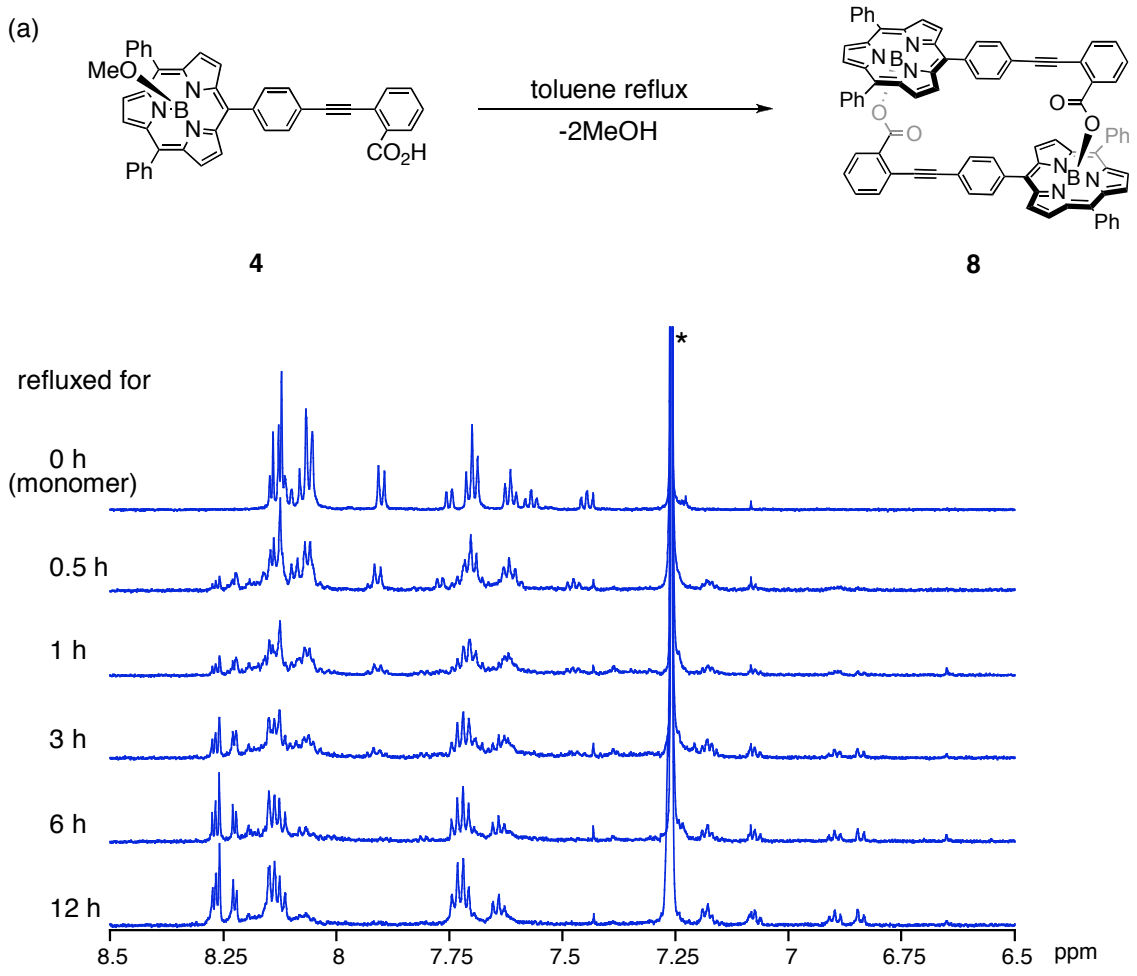
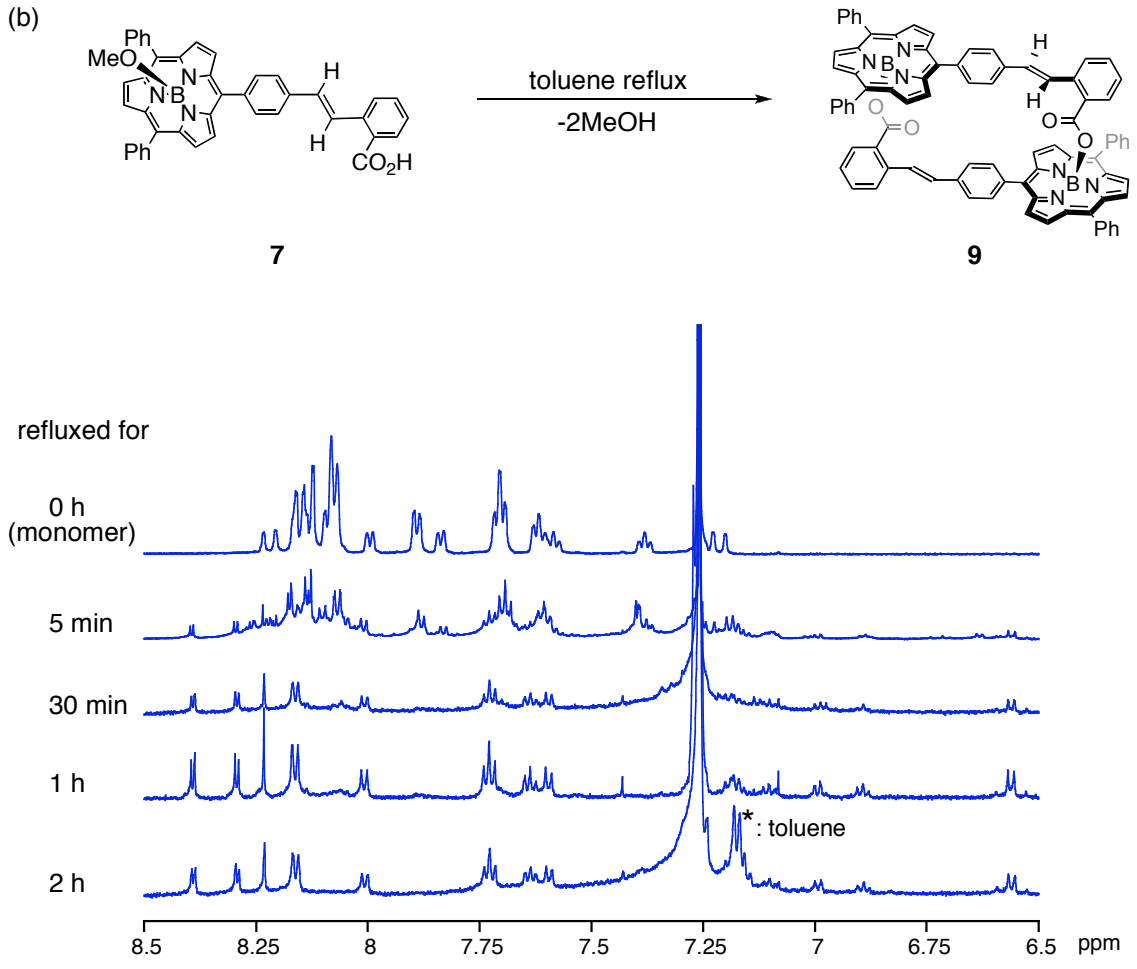


Figure S4. Monitoring of dimerization processes by ^{1}H NMR spectroscopy.

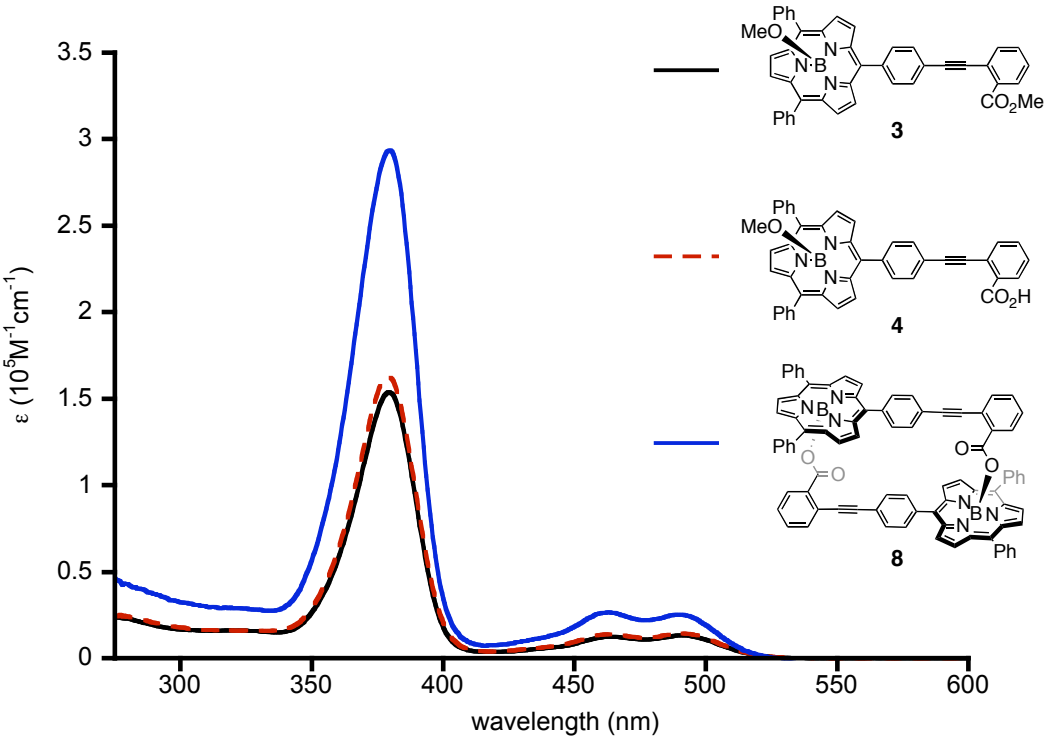


(Figure S4. continnued)



3. UV/vis absorption and fluorescence spectra

Figure S5. UV-vis absorption spectra of subporphyrins in CH_2Cl_2.



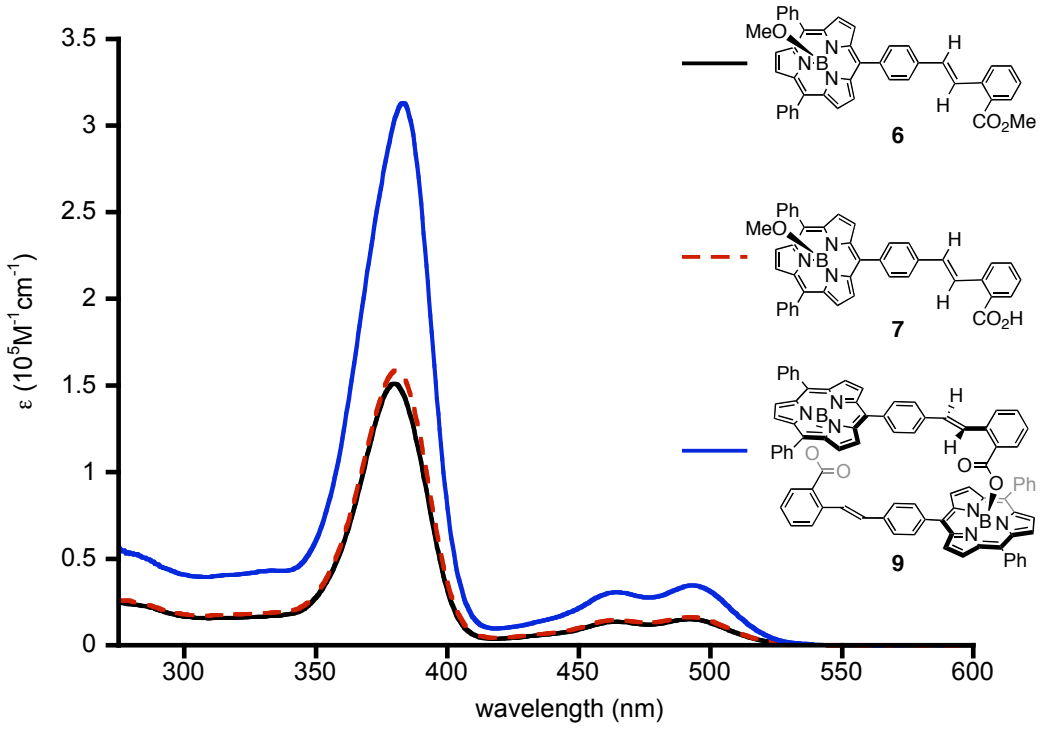
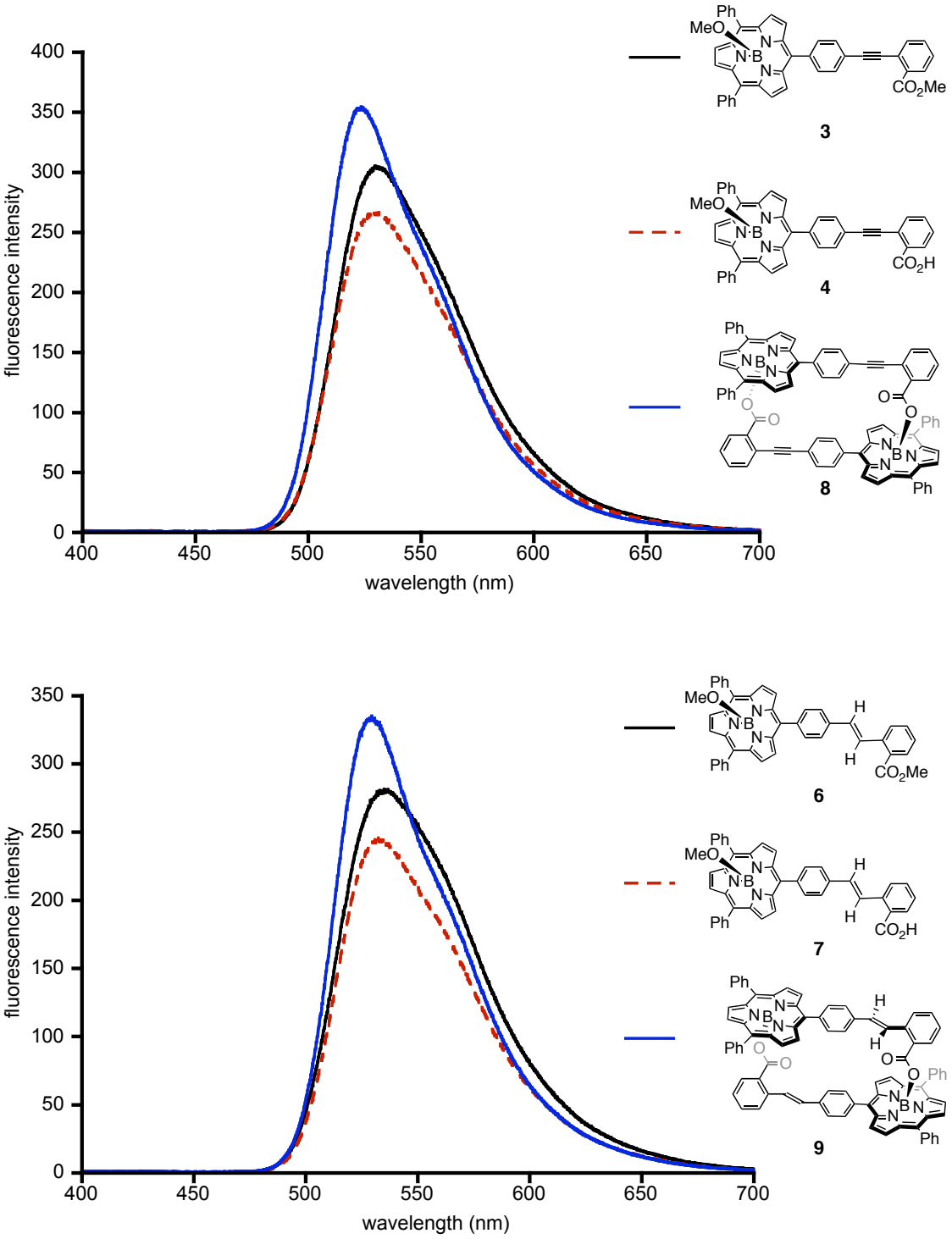
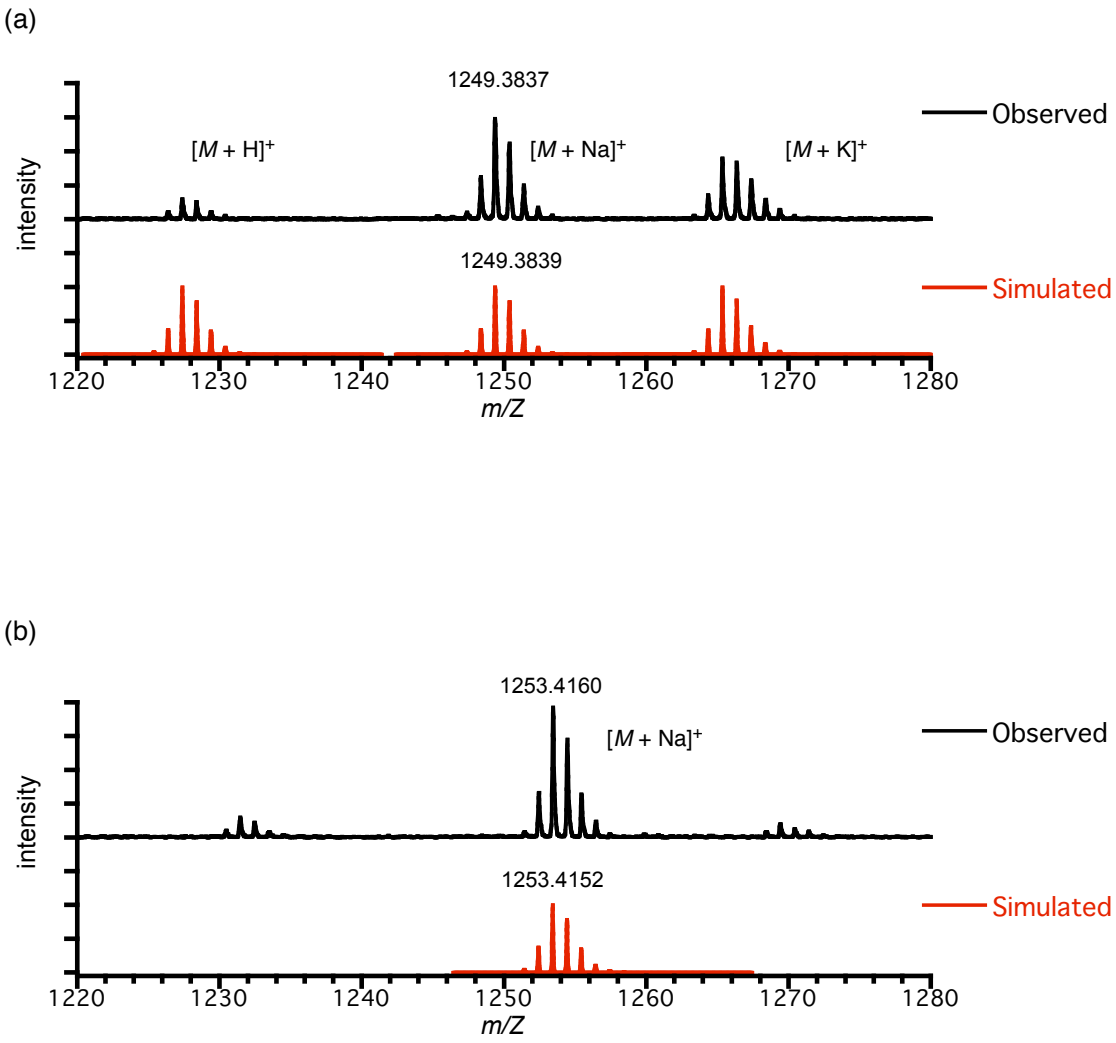


Figure S6. Fluorescence spectra of subporphyrins in CH_2Cl_2 (excited at each λ_{max} (~380 nm)).



4. ESI-TOF mass spectra

Figure S7. ESI-TOF mass spectra of dimers (a) **8** and (b) **9** (positive mode).



5. References

1 P. Szarvas, B. Györi and J. Emri *Acta. Chim. (Budapest)*, 1971, **70**, 1.

2 Y. Inokuma, Z. S. Yoon, D. Kim and A. Osuka, *J. Am. Chem. Soc.,* 2007, **129**, 4747.