Supporting Information

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SI Text

The following are detailed synthetic procedures and characterization data for all intermediate compounds and tetrakisporphyrin **2**.

10-(4-Ethoxycarbonylphenyl)-5,15-diphenylporphyrin. To a solution of 10-bromo-5,15-diphenylporphyrin **3** (950 mg, 1.75 mmol) and ethoxycarbonylphenylboronic acid (509 mg, 2.62 mmol) in toluene (20 mL) were added 2 M aqueous Na_2CO_3 (10 mL), ethanol (12 mL), and $Pd(PPh_3)_4$ (102 mg, 0.076 mmol). The mixture was heated at 60 °C for 12 h. The resulting mixture was poured into aqueous NH_4Cl, and the aqueous layer was extracted with $CHCl_3$. The organic layer was washed with aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. After filtration and concentration, the resulting purple solid was purified by column chromatography on silica gel (90% CH_2Cl_2-hexane) to give the purple solid (685 mg, 64%): melting point (mp) 278 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.25 (s, 1H), 9.36 (d, 2H, *J* = 4.8 Hz), 9.03 (d, 2H, *J* = 4.8 Hz), 8.92 (d, 2H, *J* = 4.8 Hz), 8.82 (d, 2H, *J* = 4.8 Hz), 8.45 (d, 2H, *J* = 8.1 Hz), 8.31 (d, 2H, *J* = 8.1 Hz), 8.20–8.26 (m, 4H), 7.75–7.85 (m, 6H), 4.59 (q, 2H, *J* = 6.9 Hz), 1.56 (t, 3H, *J* = 6.9 Hz), −3.00 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 147.2, 141.6, 134.6, 134.4, 131.4, 131.0, 129.9, 127.7, 126.9, 119.8, 119.0, 105.1, 61.3, 14.5. IR (KBr): 2,978, 1,715, 1,605, 1,557, 1,479, 1,439, 1,404, 1,272, 1,177, 1,108, 1,024, 1,001, 961, 849, 798, 740, 704 cm^{-1}. HR-MS (FAB; M + H^+) calculated for $C_{41}H_{31}N_4O_2$, 611.2447, found 611.2433.

10-(4-Ethoxycarbonylphenyl)-20-iodo-5,15-diphenylporphyrin 4. To a solution of 10-(4-ethoxycarbonylphenyl)-5,15-diphenylporphyrin (688 mg, 1.13 mmol) in chloroform (100 mL) were added iodine (430 mg, 1.69 mmol), $(CF_3CO_2)_2IPh$ (485 mg, 1.13 mmol), and pyridine (0.50 mL, 6.20 mmol). After being stirred for 12 h, the reaction mixture was poured into aqueous $Na_2S_2O_3$, and the aqueous layer was extracted with chloroform. The combined organic layer was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. After filtration and concentration, the crude product was purified by column chromatography on silica gel (80% CH_2Cl_2-hexane) to give the purple solid (789 mg, 95%): mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.98 (d, 2H, *J* = 5.1 Hz), 8.87 (d, 2H, *J* = 5.1 Hz), 8.80 (d, 2H, *J* = 4.8 Hz), 8.74 (d, 2H, *J* = 4.8 Hz), 8.43 (d, 2H, *J* = 8.4 Hz), 8.26 (d, 2H, *J* = 8.4 Hz), 8.18 (dd, 4H, *J* = 7.5, 1.5 Hz), 7.70–7.85 (m, 6H), 4.57 (q, 2H, *J* = 7.2 Hz), 1.519 (t, 3H, *J* = 7.2 Hz), −2.72 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 146.5, 141.7, 134.5, 134.4, 131.8, 130.0, 127.9, 126.7, 121.1, 119.7, 79.1, 61.3, 14.5. IR (KBr) 2,979, 1,716, 1,605, 1,472, 1,269, 1,176, 1,099, 1,022, 962, 796, 720, 700 cm^{-1}. HR-MS (FAB; M + H^+) calculated for $C_{41}H_{30}N_4O_2I$ 737.1413, found 737.1390.

10-(4-Ethoxycarbonylphenyl)-20-(3-nitrophenyl)-5,15-diphenylporphyrin. To a solution of 5-iodo-5,15-diphenylporphyrin **4** (743 mg, 1.01 mmol), 3-nitrophenylboronic acid (337 mg, 2.02 mmol) in toluene (30 mL) were added 2 M Na_2CO_3 (10 mL), EtOH (12 mL), and $Pd(PPh_3)_4$ (118 mg, 0.10 mmol). The mixture was heated for 12 h. The cooled mixture was poured into aqueous NH_4Cl, and the aqueous layer was extracted with chloroform. The organic layer was dried over Na_2SO_4. After filtration and concentration, the crude produce was purified by column chromatography on silica gel (50% CH_2Cl_2-hexane) to give the product (637 mg, 86%: mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (t, 1H, *J* = 2.1 Hz), 8.90 (d, 2H, *J* = 4.8 Hz), 8.88 (d, 2H, *J* = 4.8 Hz), 8.81 (d, 2H, *J* = 4.8 Hz), 8.73 (d, 2H, *J* = 4.8 Hz), 8.68 (dd, 1H, *J* = 7.8, 2.1 Hz), 8.56 (dd, 4H, *J* = 7.8, 2.1 Hz), 8.46 (d, 2H, *J* = 8.1 Hz), 8.306 (d, 2H, *J* = 8.1 Hz), 8.21 (d, 4H, *J* = 6.0 Hz), 7.955 (t, 1H, *J* = 7.8 Hz), 7.70–7.85 (m, 6H), 4.58 (q, 2H, *J* = 7.2 Hz), 1.55 (t, 3H, *J* = 7.2 Hz), −2.79 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 146.9, 146.7, 143.8, 141.7, 139.7, 134.5, 131.5, 130.0, 128.3, 127.9, 127.6, 126.8, 122.9, 120.8, 119.4, 116.7, 61.4, 14.5. IR (KBr) 3,055, 2,978, 1.715, 1,605, 1,530, 1,473, 1,440, 1,401, 1,365, 1,346, 1,270, 1,177, 1,098, 1,022, 1,000, 980, 968, 798, 751, 727, 700 cm^{-1}. HR-MS (FAB; M + H^+) calculated for $C_{47}H_{34}N_5O_4$ 732.2611, found 732.2604.

10-(4-Ethoxycarbonylphenyl)-20-(3-aminophenyl)-5,15-diphenylporphyrin. 10-(4-ethoxycarbonylphenyl)-20-(3-nitrophenyl)-5,15-diphenylporphyrin (666 mg, 0.91 mmol) was dissolved in EtOH (60 mL), chloroform (5 mL), and concentrated HCl (5 mL) was added $SnCl_2{\cdot}2H_2O$ (1.0 g, 3.90 mmol). After being stirred at 90 °C for 6 h, the cooled mixture was poured into aqueous NaOH, and the pH value of the aqueous layer was adjusted to >10. The aqueous layer was extracted with $CHCl_3$. The organic layer was washed with brine and dried over Na_2SO_4. After filtration and concentration, the resulting purple solid was purified by column chromatography on silica gel (CH_2Cl_2) to give the purple solid (600 mg, 94%): mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.97 (d, 2H, *J* = 4.8 Hz), 8.88 (d, 2H, *J* = 4.8 Hz), 8.86 (d, 2H, *J* = 4.8 Hz), 8.81 (d, 2H, *J* = 4.8 Hz), 8.47 (d, 2H, *J* = 8.4 Hz), 8.33 (d, 2H, *J* = 8.4 Hz), 8.20–8.26 (m, 4H) 7.65–7.82 (m, 6H), 7.63 (ddd, 1H, *J* = 7.8, 2.1, 1.2), 7.56 (t, 1H, *J* = 2.1 Hz), 7.51 (t, 1H, *J* = 7.8 Hz), 7.08 (ddd, 1H, *J* = 7.8, 2.1, 1.2 Hz), 4.60 (q, 2H, *J* = 7.2 Hz), 3.91 (bs, 2H), 1.57 (t, 3H, *J* = 7.2 Hz), −2.76 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 147.0, 144.5, 143.0, 142.0, 134.5, 131.5, 129.9, 127.8, 127.7, 127.3, 126.7, 125.9, 122.0, 120.8, 120.3, 118.5, 114.5, 114.4, 110.6, 61.3, 14.5. IR (KBr) 3,046, 1,716, 1,605, 1,473, 1,348, 1,272, 1,178, 1,108, 970, 799, 727, 700 cm^{-1}. HR-MS (FAB; M^+) calculated for $C_{47}H_{35}N_5O_2$ 701.2791, found 701.2819.

10-(3-Nitrophenyl)-5,15-diphenylporphyrin. To a solution of 10-bromo-5,15-diphenylporphyrin **3** (430 mg, 0.790 mmol) and 3-nitrophenylboronic acid (224 mg, 1.34 mmol) in toluene (13 mL) were added 2 M Na_2CO_3 (8 mL), ethanol (9 mL), and $Pd(PPh_3)_4$ (36 mg, 0.031 mmol). The mixture was heated at 70 °C for 12 h. The cooled reaction mixture was added in aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After filtration and concentration, the resulting purple solid was purified by column chromatography on silica gel (90% CH_2Cl_2-hexane) to give the purple solid (340 mg, 73%): mp 295–300 °C. 1H NMR (300 MHz, CDCl3) δ 10.3 (s, 1H), 9.37 (d, 2H, *J* = 4.8 Hz), 9.08 (t, 1H, *J* = 2.1 Hz), 9.05 (d, 2H, *J* = 4.8 Hz), 8.95 (d, 2H, *J* = 4.8 Hz), 8.75 (d, 2H, *J* = 4.8 Hz) 8.68 (ddd, 1H, *J* = 7.8, 2.4, 1.2 Hz), 8.54 (dt, 1H, *J* = 7.8, 1.2 Hz), 8.26 (s, 1H), 8.20–8.25 (m, 4H), 7.94 (t, 1H, *J* = 7.8 Hz), 7.75–7.85 (m, 6H), −3.01 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 144.3, 141.5, 139.6, 134.7, 134.6, 131.6, 131.4, 130.5, 128.2, 127.8, 127.4, 126.9, 126.8, 122.9, 120.1, 116.7, 105.5. IR (KBr) 3,078, 1,529, 1,480, 1,439, 1,404, 1,349, 967, 957, 795, 752, 727, 701 cm^{-1}. HR-MS (FAB; M + H^+) calculated for $C_{38}H_{26}N_5O_2$ 584.2087, found 584.2087.

10-(3-Aminophenyl)-5,15-diphenylporphyrin 6. 10-(3-nitrophenyl)-5,15- diphenylporphyrin (100 mg, 0.17 mmol) was dissolved in MeOH (2.5 mL) and concentrated HCl (10 mL). $SnCl_2{\cdot}2H_2O$

(226 mg, 0.88 mmol) was added to the mixture and heated at 70 °C for 2 h. The cooled mixture was poured into aqueous NaOH, and the pH value of the aqueous layer was adjusted to >10. The aqueous layer was extracted with $CHCl_3$. The organic layer was washed with brine and dried over Na_2SO_4. After filtration and concentration, the resulting purple solid was purified by column chromatography on silica gel (70% CH_2Cl_2-hexane) to give the purple solid (84 mg, 88%): mp >300 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 10.22 (s, 1H), 9.34 (d, 2H, J = 4.5 Hz), 9.02 (d, 2H, J = 4.5 Hz), 8.98 (d, 2H, J = 4.8 Hz), 8.89 (d, 2H, J = 4.8 Hz), 8.20–8.30 (m, 4H), 7.75–7.85 (m, 6H), 7.63 (dt, 1H, J = 7.5, 2.1 Hz), 7.55 (t, 1H, J = 2.1 Hz), 7.52 (t, 1H, J = 7.5 Hz), 7.11 (dd, 1H, J = 7.5, 2.1 Hz), 3.9 (s, 2H), −3.02 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 145.9, 144.3, 143.5, 141.8, 134.7, 131.6, 131.3, 130.6, 127.7, 127.2, 126.8, 125.9, 121.9, 120.7, 119.5, 114.3, 104.7. IR (KBr) 3,053, 1,615, 1,594, 1,478, 1,440, 1,402, 1,343, 970, 955, 795, 776, 746, 724, 697 cm^{-1}. HR-MS (FAB; M + H^+) calculated for $C_{38}H_{28}N_5$ 554.2345, found 554.2338.

Methyl 6-[3-(10,20-diphenylporphyrin-5-yl)-phenylcarbamoyl]-pyridine-2-carboxylate 7. To a solution of 6-methoxycarbonylpicolinic acid chloride (162 mg, 0.81 mmol) in THF (3 mL) was added a solution of 6 (330 mg, 0.60 mmol) and pyridine (0.10 mL, 1.25 mmol) in THF (9 mL) at 0 °C. After being stirred overnight, the reaction mixture was poured into aqueous $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After filtration and concentration, the resulting purple solid was purified by column chromatography on silica gel (10% ethylacetate-CH_2Cl_2) to give the purple solid (395 mg, 92%): mp >300 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 10.24 (s, 1H), 10.24 (s, 1H), 9.36 (d, 2H, J = 4.8 Hz), 9.06 (d, 2H, J = 4.8 Hz), 8.90–8.95 (ABq, 4H), 8.56 (t, 1H, J = 1.8 Hz), 8.47 (d, 1H, J = 7.5 Hz), 8.30–8.40 (m, 2H), 8.20–8.30 (m, 2H), 8.00 (d, 1H, J = 7.5 Hz), 7.77 (t, 1H, J = 7.5 Hz), 7.70–7.85 (m, 7H), 7.45 (d, 1H, J = 7.8 Hz), 7.08 (t, 1H, J = 7.8 Hz), 3.77 (s, 3H), −3.13 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 160.7, 148.2, 146.9, 145.7, 143.7, 143.1, 141.7, 136.3, 134.7, 131.3, 130.8, 130.4, 127.7, 126.9, 126.8, 125.6, 125.1, 123.5, 119.8, 119.6, 119.2, 104.7, 52.4. IR (KBr) 3,055, 2,949, 1,727, 1,693, 1,603, 1,538, 1,481, 1,438, 1,404, 1,342, 1,321, 1,296, 1,232, 1,190, 1,154, 1,076, 999, 970, 956, 930, 844, 797, 731, 699 cm^{-1}. HR-MS (FAB; M^+) calculated for $C_{46}H_{32}N_6O_3$ 716.2536, found 716.2513.

6-[3-(10,20-Diphenylporphyrin-5-yl)-phenylcarbamoyl]-pyridine-2-carboxylic acid. A mixture of **7** (200 mg, 0.28 mmol), KOH (200 mg, 3.57 mmol) in THF-MeOH-H_2O (45 mL, 4:1:1) was stirred for 30 min. at 0 °C. The resulting mixture was poured into water, and the pH value of the aqueous layer was adjusted to ≈3. The aqueous layer was extracted with $CHCl_3$, and the organic layer was dried over Na_2SO_4. After filtration and concentration gave the purple solid (165 mg, 84%): mp 287–290 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H), 9.63 (s, 1H), 9.26 (d, 2H, J = 4.6 Hz), 9.01 (d, 2H, J = 4.6 Hz), 8.82 (d, 2H, J = 4.6 Hz), 8.77 (d, 2H, J = 4.6 Hz), 8.41 (bs, 1H), 8.34 (bs, 2H), 8.199 (bs, 2H), 7.94 (d, 2H, J = 7.7 Hz), 7.75 (bs, 6H), 7.60 (t, 1H, J = 7.7 Hz), 7.40 (br, 1H), 7.01 (br, 1H), 6.64 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 161.0, 147.2, 146.6, 145.3, 144.1, 142.6, 141.2, 136.6, 135.6, 134.8, 131.1, 130.7, 130.6, 127.7, 126.8, 126.3, 124.7, 123.8, 119.8, 119.6, 119.5, 104.7. IR (KBr) 3,046, 1,732, 1,684, 1,585, 1,539, 1,481, 1,456, 1,438, 1,405, 1,342, 1,236, 1,154, 1,073, 1,000, 970, 956, 846, 798, 730, 700 cm^{-1}. HR-MS (FAB; M^+) calculated for $C_{45}H_{30}N_6O_3$ 702.2379, found 702.2362.

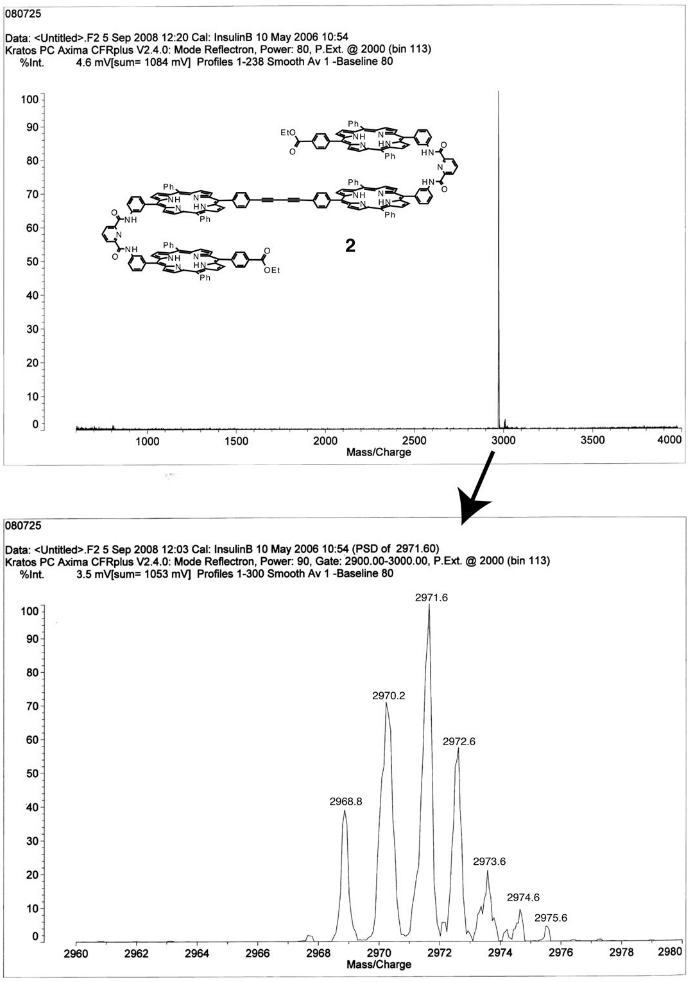
6-[3-(10,20-Diphenylporphyrin-5-yl)phenyl]-2-[3-{15-(4-ethoxycarbonylphenyl)-10,20-diphenylporphyrin-5-yl}phenyl]pyridine dicarboxy amide 8. To a solution of 6-[3-(10,20-diphenylporphyrin-5-yl)-phenylcarbamoyl]-pyridine-2-carboxylic acid (58 mg, 0.083 mmol), and **6** (70 mg, 0.126 mmol) in CH_2Cl_2 (8 mL) was added a solution of EDAC (30 mg, 0.156 mmol), pyridine (0.2 mL, 2.50 mmol) and a catalytic amount of DMAP. After being stirred for 3 days, the reaction mixture was diluted with CH_2Cl_2. The organic layer was washed with $NaHCO_3$, and dried over Na_2SO_4. After filtration and concentration, the crude mixture was purified by column chromatography on silica gel (ethylacetate:CH_2Cl_2:hexane = 4:50:50) to give a purple solid (95 mg, 82%): mp >300 °C. ^1H NMR (500 MHz, 20 mM, $CDCl_3$) δ 10.12 (s, 1H), 9.25 (d, 2H, J = 4.6 Hz), 8.96 (d, 2H, J = 4.6 Hz), 8.82 (d, 2H, J = 4.6 Hz), 8.80 (d, 2H, J = 4.6 Hz), 8.70–8.80 (ABq, 4H), 8.71 (s, 4H), 8.46 (d, 1H, J = 7.4 Hz), 8.44 (d, 1H, J = 7.7 Hz), 8.44 (s, 1H), 8.39 (d, 1H, J = 7.7 Hz), 8.36 (s, 1H), 8.29 (d, 1H, J = 7.4 Hz), 8.21 (d, 2H, J = 7.4 Hz), 8.14 (d, 2H, J = 7.4 Hz), 8.09 (d, 2H, J = 7.4 Hz), 8.07 (d, 2H, J = 7.4 Hz), 7.77 (d, 2H, J = 7.3 Hz), 7.64 (t, 2H, J = 7.4 Hz), 7.63 (t, 2H, J = 7.4 Hz), 7.40–7.60 (m, 10H), 7.37 (t, 1H, J = 7.3 Hz), 7.35 (t, 1H, J = 7.3 Hz), 5.53 (br, 1H), 5.42 (br, 1H), 4.54 (q, 2H, J = 7.3 Hz), 4.50 (br, 1H), 1.52 (t, 3H, J = 7.3 Hz), −3.19 (s, 2H), −3.45 (s, 2H). ^{13}C NMR (125 MHz, 20 mM, $CDCl_3$) δ 166.8, 159.6, 159.4, 146.9, 145.2, 143.1, 142.6, 141.8, 141.5, 135.6, 135.4, 135.3, 134.7, 134.6, 134.4, 131.3, 131.0, 129.9, 127.8, 127.6, 127.5, 126.9, 126.7, 126.6, 125.8, 125.7, 122.1, 120.3, 120.3, 119.6, 119.3, 119.1, 118.7, 104.9, 61.2, 14.5. IR (KBr) 3,646, 1,714, 1,686, 1,602, 1,530, 1,473, 1,439, 1,422, 1,402, 1,364, 1,345, 1,306, 1,269, 1,177, 1,154, 1,098, 1,071, 970, 930, 872, 844, 797, 748, 727, 700 cm^{-1}. HR-MS (FAB; M^+) calculated for $C_{92}H_{63}N_{11}O_4$ 1385.5064, found 1385.5057.

6-[3-(15-Iodo-10,20-diphenylporphyrin-5-yl)phenyl]-2-[3-{15-(4-ethoxycarbonylphenyl)-10,20-diphenylporphyrin-5-yl}phenyl]pyridine dicarboxy amide. A solution of **8** (90 mg, 0.065 mmol), iodine (26 mg, 0.10 mmol), pyridine (0.15 mL, 1.87 mmol), $(CF_3CO_2)_2IPh$ (28 mg, 0.065 mmol) in $CHCl_3$ was stirred overnight. The reaction mixture was poured into aqueous $Na_2S_2O_3$, and the aqueous layer was extracted with $CHCl_3$. The organic layer was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. After filtration and concentration, the resulting crude product was purified by column chromatograpy on silica gel (10% ethylacetate-CH_2Cl_2) to give the desired idodide as a purple solid (89 mg, 91%): mp >300 °C. ^1H NMR (500 MHz, 5 mM, $CDCl_3$) δ 9.65 (d, 2H, J = 4.9 Hz), 8.81 (ABq, 4H), 8.79 (d, 2H, J = 4.9 Hz), 8.70 (s, 4H), 8.55–8.70 (ABq, 4H), 8.47 (d, 1H, J = 7.9 Hz), 8.45 (d, 1H, J = 7.9 Hz), 8.37 (bs, 1H), 8.36 (d, 1H, J = 7.9 Hz), 8.29 (d, 1H, J = 7.9 Hz), 8.05–8.15 (m, 5H), 8.04 (d, 2H, J = 6.4 Hz), 7.84 (d, 1H, J = 7.3 Hz), 7.76 (d, 1H, J = 7.3 Hz), 7.45–7.70 (m, 14H), 7.35–7.45 (m, 2H), 6.19 (br, 2H), 5.33 (br, 1H), 4.56 (q, 2H, J = 7.1 Hz), 1.54 (t, 3H, J = 7.1 Hz), −3.09 (s, 2H), −3.14 (s, 2H). ^{13}C NMR (125 MHz, 20 mM, $CDCl_3$) δ 166.87, 159.30, 159.1, 146.9, 144.9, 142.5, 142.2, 141.8, 141.5, 135.4, 135.3, 134.6, 134.4, 130.9, 129.9, 127.9, 127.8, 127.7, 127.6, 127.0, 126.6, 125.6, 125.5, 121.7, 120.8, 120.2, 119.9, 119.2, 119.0, 118.8, 78.8, 61.3, 14.5. IR (KBr) 3,735, 1,715, 1,684, 1,602, 1,526, 1,471, 1,438, 1,399, 1,341, 1,270, 1,217, 1,178, 1,099, 1,072, 1,021, 999, 970, 798, 749, 725, 700 cm^{-1}. HR-MS (FAB; M^+) calculated for $C_{92}H_{62}IN_{11}O_4$ 1511.4031, found 1511.4025.

2-[3-{15-(Ethoxycarbonylphenyl)-10,20-diphenyl}-10,20-diphenylporphyrin-5-yl]phenyl]-6-[3-(15-(4ethynylphenyl)-10,20-diphenylporpyrin-5-yl)-phenyl]pyrindine dicarboxy amide (9). To a solution of the above iodide (80.0 mg, 0.053 mmol), 4-trimethylsilylethynylphenylboronic acid (26.0 mg, 0.119 mmol), 2M Cs_2CO_3 (1 mL), and EtOH (1.2 mL) in toluene (7 mL) was added a solution of $Pd(PPh_3)_4$ (40 mg, 0.034 mmol) in toluene (7 mL). The resulting mixture was heated at 80 °C overnight. The cooled mixture was diluted with CH_2Cl_2 and washed with aqueous NH_4Cl. The organic layer was dried over Na_2SO_4. After filtration and concentration, the crude product (72 mg, 88%) was obtained. This product was dissolved in THF (18 mL). TBAF (24 mg, 0.092 mmol) was added to the solution and stirred at room temperature for 2 h. The resulting mixture was poured into brine, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4. After filtration and concentration, a residue was purified by column chromatography on silica gel (20% ethylacetate-CH_2Cl_2) to give desired product **9** (43 mg, 55%) as a purple solid: mp >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65–8.85 (m, 16H), 8.47 (bs, 1H), 8.44 (d, 1H, *J* = 8.5 Hz), 8.36 (d, 1H, *J* = 8.5 Hz), 8.30 (d, 1H, *J* = 8.5 Hz), 8.27 (d, 1H, *J* = 8.5 Hz), 8.00–8.25 (m, 10H), 7.45–7.90 (m, 21H), 6.26 (br, 2H), 5.48 (br, 1H), 4.52 (q, 2H, *J* = 7.1 Hz), 3.22 (s, 1H), 1.51 (t, 3H, *J* = 7.1 Hz), −3.21 (bs, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 159.0, 146.8, 144.7, 142.7, 142.5, 141.7, 135.5, 134.6, 134.5, 134.4, 131.2, 130.4, 129.9, 127.8, 127.6, 126.9, 126.6, 125.6, 125.5, 121.5, 120.2, 120.1, 119.2, 119.1, 119.0, 118.9, 118.8, 83.5, 78.1, 61.2, 14.4. IR (KBr) 3,312, 3,052, 1,715, 1,687, 1,603, 1,532, 1,472, 1,439, 1,401, 1,364, 1,348, 1,271, 1,222, 1,179, 1,099, 1,073, 1,021, 1,000, 970, 799, 751, 728, 700 cm^{-1}. HR-MS (FAB; M$^+$) calculated for $C_{100}H_{67}N_{11}O_4$ 1485.5377, found 1485.5371.

2-[3-{Zinc(II)-15-(4-ethoxycarbonylphenyl)-10,20,diphenylporphyrin-5-yl}-phenyl]-6-[3-{zinc(II)-15-(4-ethynylphenyl)-10,20-diphenylporphyrin-5-yl}phenyl]-pyridine dicarboxy amide. To a solution of bisporphyrin **9** (36.5 mg, 0.025 mmol) in $CHCl_3$-EtOH (5 mL, 2:1) was added $Zn(OAc)_2$ (10.0 mg, 0.054 mmol). After being stirred for 1 h at 25 °C, the solvents were removed in vacuo. The residue was purified by column chromatography on silica gel (10% AcOEt-CH_2Cl_2) to give a desired product (39 mg, 96%) as a purple solid: mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00–9.00 (m, 52H), 6.60 (br, 2H), 5.40 (br, 1H), 4.30 (Br, 2H), 1.50 (br, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 157.9, 149.7, 149.5, 149.2, 149.0, 147.9, 147.7, 143.5, 142.9, 142.4, 134.7, 134.5, 134.2, 132.3, 131.9, 131.7, 131.2, 130.9, 130.3, 127.3, 126.5, 121.2, 120.7, 119.9, 119.6, 117.8, 117.6, 83.7, 78.1, 61.0, 14.4. IR (KBr) 3,291, 3,051, 1,690, 1,604, 1,524, 1,482, 1,440, 1,338, 1,272, 1,206, 1,177, 1,100, 1,070, 1,001, 795, 753, 718, 701 cm^{-1}. HR-MS (FAB; M$^+$) calculated for $C_{100}H_{63}N_{11}O_4Zn_2$ 1609.3647, found 1609.3625.

Tetrakisporphyrin 2. A solution of the bisporphyrin zinc complex (39.0 mg, 0.024 mmol) and $Cu(OAc)_2$ (44.0 mg, 0.24 mmol) in pyridine (3 mL) was heated at 60 °C for 17 h. The cooled reaction mixture was diluted with CH_2Cl_2 (20 mL). The organic layer was washed with aqueous $NaHCO_3$ and brine. EtOH (3 mL) was added to the organic layer, which was acidified with 3M HCl (3 mL). After being stirred for 1.5 h, the reaction mixture was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. After filtration and concentration, a residue was purified by column chromatography on silica gel (20% ethylacetate-CH_2Cl_2) to give desired product **2** (30 mg, 84%) as a purple solid: mp >300 °C. IR (KBr) 3,313, 2,922, 2,851, 2,359, 1,683, 1,604, 1,539, 1,472, 1,179, 1,009, 1,074, 1,021, 1,000, 970, 799, 728, 701 cm^{-1}. HR-MS (FAB; M$^+$) calculated for $C_{200}H_{132}N_{22}O_8$ 2969.0598, found 2969.0588.



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080725

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Fig. S1. MALDI-TOF mass spectra of **2**.

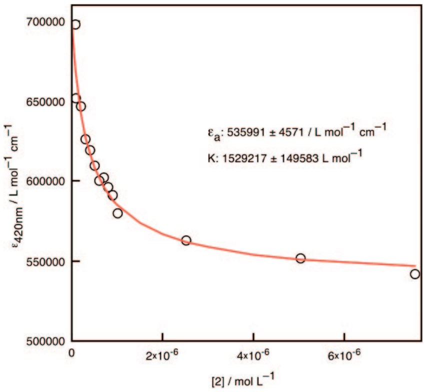

Fig. S2. Plots of the concentrations of **2** versus the apparent extinction coefficients and the theoretical curve (in red) determined by nonlinear curve-fitting analysis based on isodesmic model.

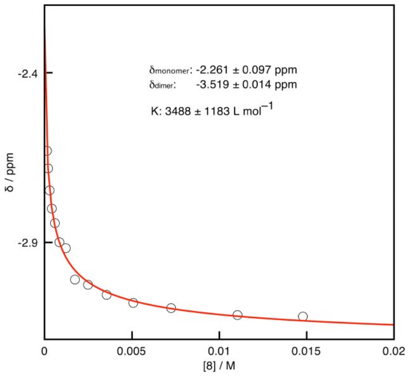

Fig. S3. Plots of the concentrations of **8** versus the chemical shifts of the N–H signal of the porphyrin unit and the theoretical curve (in red) determined by nonlinear curve-fitting analysis based on monomer–dimer equilibrium model.

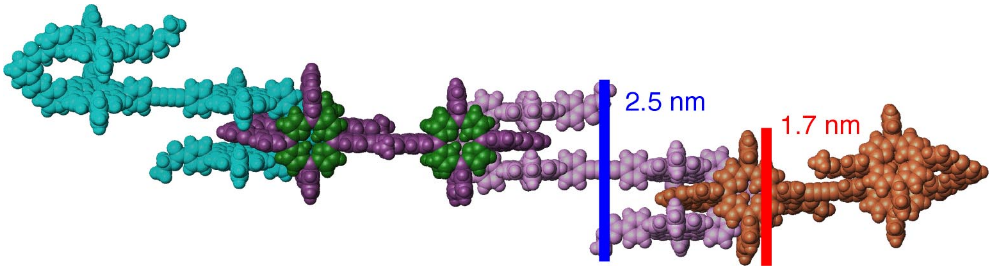

Fig. S4. Calculated structure of the tetramer of **2** by using MacroModel V9.1.