Supplementary Information

Oxidative coupling of porphyrins using copper(II) salts

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Chemicals and Materials

$Cu(ClO_4)_2$ x $6H_2O$ (Alfa Aesar, reagent grade) and $Cu(BF_4)_2$ x $6H_2O$ (Strem Chemicals, 99%) were partially dehydrated under vacuum and stored in a desiccator. Acetonitrile (Omnisolv grade) was obtained from VWR and stored with molecular sieves. Dichloromethane, tetrahydrofuran, and hexanes were distilled prior to use. All other chemicals were obtained from commercials sources and used without further purification. Silica gel chromatography was performed using 230-400 mesh silica gel (Silicycle, Siliflash F60).

Analytical Methods

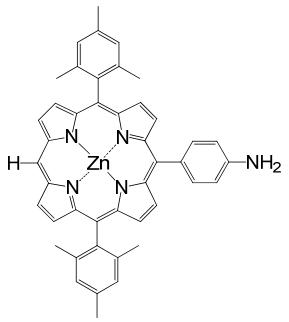
Absorption spectra were measured on a Shimadzu UV-3101PC UV–Visible-NIR spectrometer. Mass spectrometry was performed by the MALDI-TOF method using a Voyager DE STR from Applied Biosystems with a terthiophene or diphenylbutadiene matrix. ^{1}H NMR spectra were obtained in $CDCl_3$ or pyridine-d_5 using a Varian 400 MHz or 500 MHz instrument. HPLC-gel permeation chromatography was performed on an Agilent 1200 series HPLC with UV-Visible diode-array detector using a 79911-GP-MXC 5 μm mixed-C column. A calibration using polystyrene standards in THF with 1 mL/min elution was used for analysis. Dilute 30 μL samples of porphyrin polymer in THF were used for characterization. GPC analysis performed using Agilent ChemStation Rev.B.03.01 with GPC software add-on Rev.B.01.01.

Synthetic Procedures

The porphyrin 5-(4-aminophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin[S1] **(1)** and 5-(4-methoxycarbonylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin[S2] were synthesized as described previously.

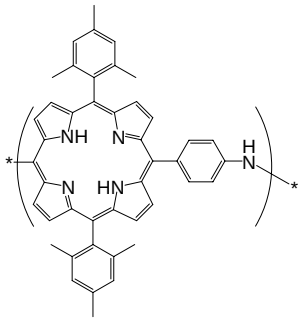
General procedure for porphyrin metallations

Metallation of porphyrins was performed by adding porphyrin and 5-10 equivalents of zinc(II) acetate dihydrate or copper(II) acetate hydrate and to a solution of 5:1 dichloromethane / methanol. The solution was heated for 30 min and then allowed to stir overnight under a nitrogen atmosphere. The organic layer was washed with distilled water, saturated aqueous sodium bicarbonate, and again with distilled water, and the organic layer was dried by distillation under reduced pressure. The reactions went to completion.



2

Zn(II)-5-(4-aminophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (2) was synthesized as specified by the general procedure for porphyrin metallation given above.[1]H NMR (400 MHz, $CDCl_3$) δ 10.14 (1H, s, meso-H), 9.33 (2H, d, *J*=4 Hz, β-H), 8.96 (2H, d, *J*=4 Hz, β-H), 8.90 (2H, d, *J*=4 Hz, β-H), 8.80 (2H, d, *J*=4 Hz, β-H), 7.92 (2H, d, *J*=8 Hz, Ar-H), 7.29 (1H, s, Ar-H), 6.75 (2H, d, *J*=8 Hz, Ar-H), 3.50 (2H, s, NH_2), 2.65 (6H, s, Ar-CH_3), 1.83 (12H, s, Ar-CH_3); MALDI-TOF-MS m/z calcd for $C_{44}H_{37}N_5Zn$ 699.2, obsd 699.0; UV-visible ($\lambda_{max,}$ CH_2Cl_2) 416, 544, 580 nm.

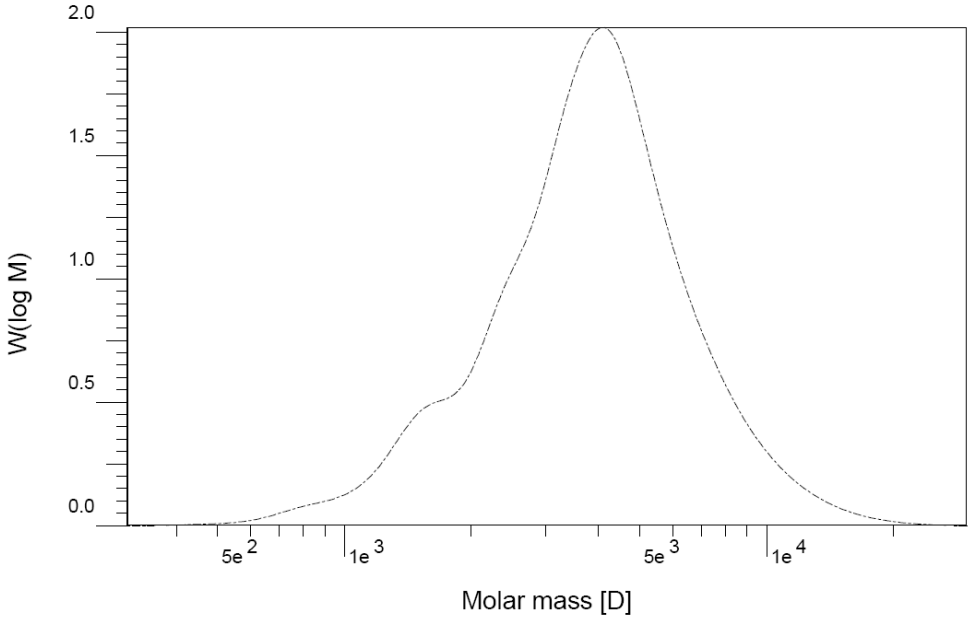


poly 2

Polymerization of 2. A mixture of 300 mg ofporphyrin monomer **2** (4.28×10^{-4} mol) in 70 mL of acetonitrile was placed under nitrogen and cooled in an ice bath. A solution of 517 mg ($1.5x10^{-3}$ mol, 3.5 equivalents) $Cu(BF_4)_2$•6 H_2O in 10 mL of acetonitrile was added. All porphyrin immediately dissolved and the solution turned green. The ice bath was removed and the reaction was stirred at room temperature for 5 h. An aqueous solution of 1.5 g potassium ferrocyanide in 25 mL distilled H_2O was added to quench the reaction and precipitate the porphyrin. The mixture was filtered and the residue washed with aqueous basic EDTA, then aqueous sodium bicarbonate, and finally distilled H_2O. The solid remaining was dissolved in 50 mL of trifluoroacetic acid and stirred under a nitrogen atmosphere for 3 h. The solution was transferred to a separatory funnel and 120 mL chloroform and 150 mL of H_2O were added. The organic layer was washed with 300 mL of saturated aqueous sodium bicarbonate and then 200 mL of distilled H_2O. The organic layer was distilled under reduced pressure. The solid obtained was dissolved in 35 mL of dichloromethane, and the porphyrin was precipitated by adding 190 mL of hexanes. The mixture was filtered to yield 196 mg of precipitated porphyrin (72%). [1]H NMR (500 MHz, $CDCl_3$) δ 9.6-8.6 (β-H), 8.0-6.8 (Ar-H, β-H from fused porphyrin impurity, N-H), 4.2-3.7 (Ar-NH_2), 2.65-2.50 (Ar-CH_3), 2.00-1.80 (Ar-CH_3), -2.25 to -2.45 (N-H); UV-visible

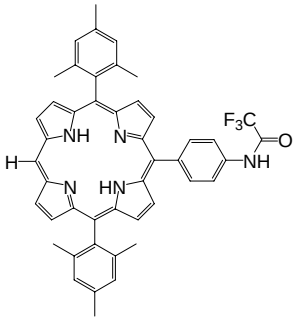
($\lambda_{max,}$ THF) 418, 523, 581, 667, 818, 1062, 1105 nm. Analysis by MALDI-TOF-MS showed a series of peaks corresponding to oligomers of the polymer of different lengths.

Figure S1. HPLC-GPC analysis of oligomeric porphyrin **poly2.**



dad1A

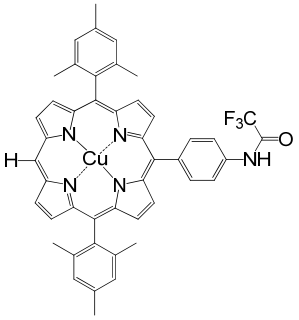
Mn :	3.1674e3	g/mol
Mw :	4.3433e3	g/mol
Mz :	5.7884e3	g/mol
Mv :	0.000000	g/mol
D :	1.3712e0	
[n]:	0.000000	ml/g
Vp :	7.7028e0	ml
Mp :	4.0758e3	g/mol
A :	1.6292e2	ml*V
10%	1.7672e3	g/mol
30%	2.9703e3	g/mol
50%	3.8791e3	g/mol
70%	4.9246e3	g/mol
90%	7.3362e3	g/mol



15

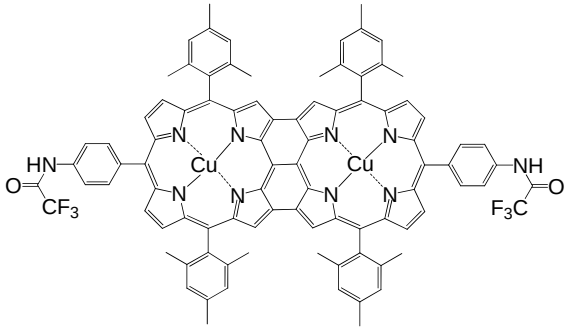
5-(4-Trifluoroacetamidophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (15). A solution of 164 mg of **1** (2.57×10^{-4} mol) in 40 mL dichloromethane and 200 µL pyridine was cooled in an ice bath under a nitrogen atmosphere. Trifluoroacetic anhydride (178 µL, 1.28×10^{-3} mol, 5 equivalents) was added and the solution was stirred for 3.5 h. The reaction mixture was washed

with saturated aqueous sodium bicarbonate solution and then H_2O to yield 180 mg (95%) **15**. ^1H NMR (400 MHz, $CDCl_3$) δ 10.12 (1H, s, meso-H), 9.26 (2H, d, *J*=4 Hz, β-H), 8.83 (2 H, d, *J*=4 Hz, β-H), 8.77 (2H, d, *J*=5 Hz, β-H), 8.75 (2H, d, *J*=4 Hz, β-H), 8.24 (1H, s, N-H), 8.23 (2H, d, *J*=7 Hz, Ar-H), 7.93 (2H, d, *J*=7 Hz, Ar-H), 7.29 (4H, s, Ar-H), 2.63 (6H, s, Ar-CH_3) 1.83 (12H, s, Ar-CH_3), -2.90 (2H, s, N-H); MALDI-TOF-MS m/z calcd for $C_{46}H_{38}F_3N_5O$ 733.3, obsd 733.4; UV-visible ($\lambda_{max,}$ CH_2Cl_2) 412, 508, 540, 583, 638 nm.

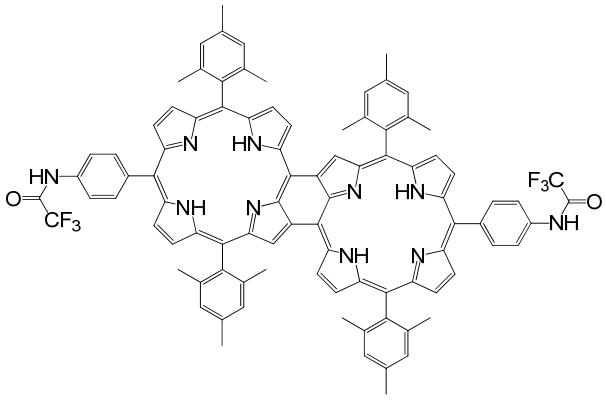


5

Cu(II)-5-(4-trifluoroacetamidophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (5) was synthesized as specified by the general procedure for porphyrin metalation described above. MALDI-TOF-MS m/z calcd for $C_{46}H_{36}CuF_3N_5O$ 794.2, obsd 794.4; UV-visible ($\lambda_{max,}$ CH_2Cl_2) 410, 534, 567 nm.



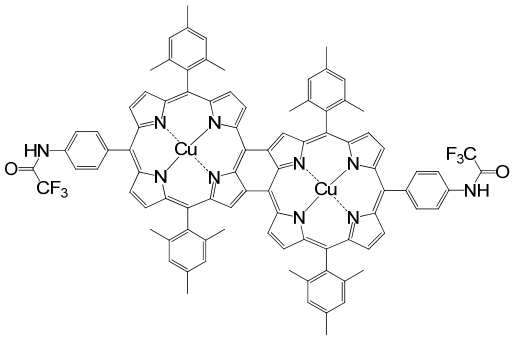
6



8

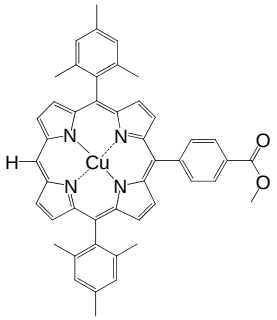
Porphyrin dimers 6 and 8. A solution of 179 mg of $Cu(ClO_4)_2$•6 H_2O (4.83×10^{-4} mol, 3.3 equivalents) in 4 mL acetonitrile was added to a mixture of 116 mg porphyrin **5** (1.46×10^{-4} mol) in 35 mL of acetonitrile. All porphyrin immediately dissolved and the solution slowly turned purple. The solution was stirred under a nitrogen atmosphere for 3.5 h. The reaction was quenched with an aqueous solution of 400 mg of potassium ferrocyanide in 40 mL of distilled H_2O, and 50 mL chloroform was added. The organic was washed three times with 50 mL of H_2O and then the solvent was removed by distillation under reduced pressure. The porphyrin was stirred in an ice cold solution of 20 mL of trifluoroacetic acid, 10 mL of chloroform, and 6.5 mL of concentrated sulfuric acid for 1.5 h. The solution was added to 50 mL of cold distilled H_2O in a separatory funnel and extracted twice with 30 mL of chloroform. The combined

organic extracts were washed with distilled H_2O, saturated aqueous sodium bicarbonate containing EDTA, and again with distilled H_2O (50 mL each). The organic layer was dried under reduced pressure. Repeated flash column chromatography using silica gel and 3:2 dichloromethane / hexanes yielded Cu-triply connected **(6)** (33 mg, 29%) and free base doubly connected **(8)** (36 mg, 34%) as the first and second major band, respectively. For **6**: MALDI-TOF-MS m/z calcd for $C_{92}H_{66}Cu_2F_6N_{10}O_2$ 1584.4, obsd 1584.6; UV-visible-NIR ($\lambda_{max,}$ CH_2Cl_2) 409, 557, 577, 911(sh), 1002 nm. For **8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (2H, d, *J*=5 Hz, β-H), 8.83 (2H, s, β-H), 8.46 (2H, d, *J*=5 Hz, β-H), 8.31 (2H, d, *J*=5 Hz, β-H), 8.26 (2H, d, *J*=5 Hz, β-H), 8.24 (2H, d, *J*=5 Hz, β-H), 8.20 (2H, d, *J*=5 Hz, β-H), 8.17 (2H, s, N-H), 8.13 (4H, d, *J*=8 Hz, Ar-H), 7.93 (4H, d, *J*=8 Hz, Ar-H), 7.31 (4H, s, Ar-H), 7.25 (4H, s, Ar-H), 2.66 (6H, s, Ar-CH_3), 2.61 (6H, s, Ar-CH_3), 2.08 (12H, s, Ar-CH_3), 1.95 (12H, s, Ar-CH_3), 0.71 (4H, s, N-H); MALDI-TOF-MS m/z calcd for $C_{92}H_{72}F_6N_{10}O_2$ 1463.6, obsd 1463.7; UV-visible-NIR ($\lambda_{max,}$ CH_2Cl_2) 424, 499, 561, 611, 739(sh), 814 nm.



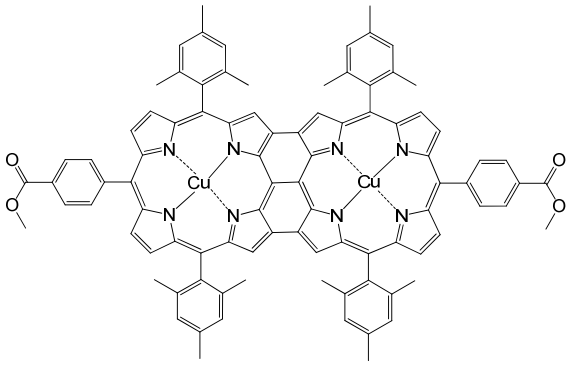
7

Porphyrin dimer 7. Dimer **7** was prepared from **8** as described by the general procedure for porphyrin metalation given above. MALDI-TOF-MS m/z calcd for $C_{92}H_{68}Cu_2F_6N_{10}O_2$ 1586.4, obsd 1586.2; UV-visible ($\lambda_{max,}$ CH_2Cl_2) 418, 487 (sh), 553, 629, 702 (sh), 768 nm.

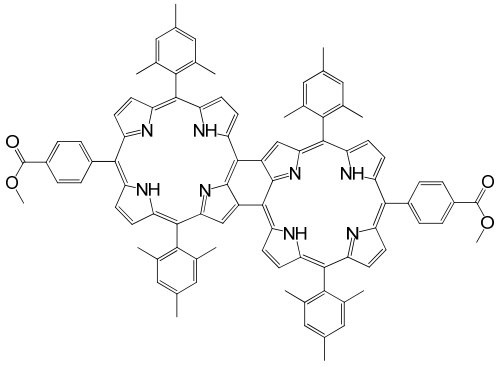


9

Cu(II)-5-(4-methoxycarbonyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (9). This material was prepared from 5-(4-methoxycarbonylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin as specified by the general procedure for porphyrin metalation given above. MALDI-TOF-MS m/z calcd for $C_{46}H_{38}CuN_4O_2$ 741.2, obsd 741.3; UV-visible ($\lambda_{max,}$ CH_2Cl_2) 410, 534, 567 nm.

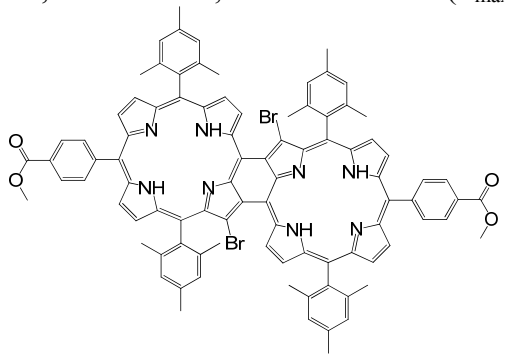


10

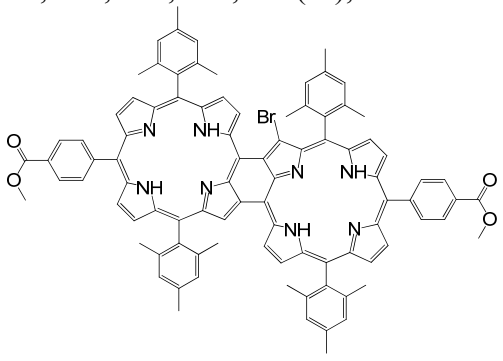


12

Porphyrin dimers 10 and 12. A solution of 200 mg of $Cu(ClO_4)_2$•6 H_2O (5.40×10^{-4} mol, 3.3 equivalents) in 5 mL of acetonitrile was added to a mixture of 123 mg of porphyrin **9** (1.65×10^{-4} mol) in 40 mL of acetonitrile. All porphyrin immediately dissolved and the solution slowly turned purple. The solution was stirred under a nitrogen atmosphere for 3 h. The reaction was quenched with an aqueous solution of 350 mg of potassium ferrocyanide in 50 mL of distilled H_2O, and 50 mL of dichloromethane were added. The organic was washed three times with 60 mL of H_2O and the solvent was distilled under reduced pressure. The porphyrin was stirred in a solution of 20 mL of trifluoroacetic acid, 10 mL of dichloromethane, and 6 mL of concentrated sulfuric acid for 30 min. The solution was then added to 50 mL of cold distilled H_2O in a separatory funnel and 30 mL of chloroform was added. The organic layer was washed with distilled H_2O, saturated aqueous sodium bicarbonate containing EDTA, and again with distilled H_2O (50 mL each). The organic layer was dried by distillation of the solvent under reduced pressure. Flash column chromatography using silica gel and 1:1 dichloromethane / hexanes yielded Cu-triply connected **(10)** (38 mg, 31%) and free base double connected **(12)** (53 mg, 47%) as the first and second major band, respectively. For **10**: MALDI-TOF-MS m/z calcd for $C_{92}H_{70}Cu_2N_8O_4$ 1478.4, obsd 1478.5; UV-visible-NIR ($\lambda_{max,}$ CH_2Cl_2) 409, 557, 577, 909 (sh), 1002 nm. For **12**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (2H, d, *J*=5 Hz, β-H), 8.83 (2H, s, β-H), 8.46 (2H, d, *J*=5 Hz, β-H), 8.37 (4H, d, *J*=8 Hz, Ar-H), 8.29 (2H, d, *J*=5 Hz, β-H), 8.24 (4H, d, *J*=5 Hz, β-H), 8.20 (2H, d, *J*=5 Hz, β-H), 8.17 (4H, d, *J*=8 Hz, Ar-H), 7.30 (4H, s, Ar-H), 7.25 (4H, s, Ar-H), 4.08 (6H, s, O-CH_3), 2.66 (6H, s, Ar-CH_3), 2.61 (6H, s, Ar-CH_3), 2.08 (12H, s, Ar-CH_3), 1.95 (12H, s, Ar-CH_3), 0.71 (4H, s, N-H); MALDI-TOF-MS m/z calcd for $C_{92}H_{76}N_8O_4$ 1357.6, obsd 1357.6; UV-visible-NIR ($\lambda_{max,}$ CH_2Cl_2) 425, 499, 561, 610, 739(sh), 812 nm.



13

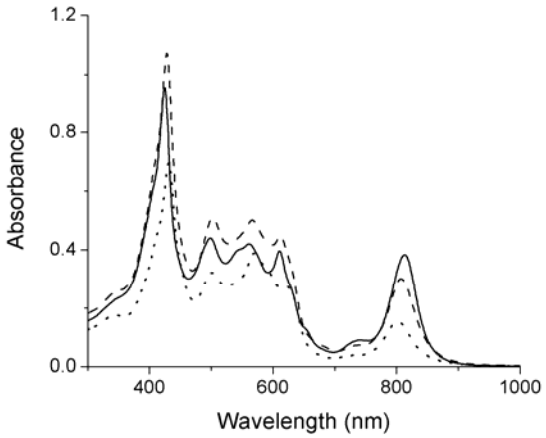


14

Bromination of 12. A solution of 34 mg of porphyrin **12** (2.5×10^{-5} mol) and 4.5 mg of N-bromosuccinimide (2.5×10^{-5} mol) in 10 mL of $CHCl_3$ was stirred at room temperature for 20 h

and then dried by distillation of the solvent under reduced pressure. The crude material was chromatographed on silica using 2:1 dichloromethane / hexanes. Dibrominated compound **13** eluted first followed by mono-brominated compound **14**, with yields of 12 mg (32%) and 10.2 mg (29%) respectively. For **13**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (2H, d, *J*=5 Hz, β-H), 8.45-8.25 (6H, br, Ar-H), 8.21 (2H, d, *J*=5 Hz, β-H), 8.20 (2H, d, *J*=5 Hz, β-H), 8.18 (2H, d, *J*=5 Hz, β-H), 8.17 (2H, d, *J*=5 Hz, β-H), 8.12 (2H, d, *J*=5 Hz, β-H), 8.01 (2H, br s, Ar-H), 7.23 (2H, br s, Ar-H), 7.16 (6H, s, Ar-H), 4.08 (6H,s, O-CH_3), 2.54 (6H,s, Ar-CH_3), 2.51 (6H, s, Ar-CH_3), 2.23 (6H, s, Ar-CH_3), 2.07 (6H, s, Ar-CH_3), 1.76 (12H, br s, Ar-CH_3), 1.74 (6H, br s, Ar-CH_3), 1.06 (2H, s, N-H), 0.58 (2H, s, N-H); ^{1}H NMR (500 MHz, pyridine-d_5) δ 9.63 (2H, d, *J*=5 Hz, β-H), 8.53 (2H, d, *J*=5 Hz, β-H), 8.49 (4H, d, *J*=5 Hz, β-H), 8.46 (4H, d, *J*=8 Hz, Ar-H), 8.42 (2H, d, *J*=5 Hz, β-H), 8.31 (2H, d, *J*=5 Hz, β-H), 8.2 (4H, br s, Ar-H), 7.45-7.22 (8H, br m, Ar-H), 4.02 (6H, s, O-CH_3), 2.61 (6H, s, Ar-CH_3), 2.60 (6H, s, Ar-CH_3), 2.51 (6H, s, Ar-CH_3), 2.31 (6H, s, Ar-CH_3), 2.08 (6H, s, Ar-CH_3), 1.94 (6H, s, Ar-CH_3), 1.45 (2H, s, N-H), 0.98 (2H, s, N-H); MALDI-TOF-MS m/z calcd for $C_{92}H_{74}Br_2N_8O_4$ 1514.4, obsd 1514.5; UV-visible-NIR ($\lambda_{max,}$ CH_2Cl_2) 431, 501, 569, 618, 802 nm. For **14**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (1H, d, *J*=5 Hz, β-H), 9.21 (1H, d, *J*=5 Hz, β-H), 8.54 (1H, s, β-H), 8.49 (1H, d, *J*=5 Hz, β-H), 8.37 (4H, d, *J*=8 Hz, Ar-H), 8.28-8.15 (13H, β-H, Ar-H), 7.23 (4H, br s, Ar-H), 7.21 (2H, br s, Ar-H), 4.083 (3H, s, O-CH_3), 4.081 (3H, s, O-CH_3), 2.60 (3H, s, Ar-CH_3), 2.58 (3H, s, Ar-CH_3), 2.56 (6H, s, Ar-CH_3), 2.3-1.7 (12H, br s, Ar-CH_3), 2.01 (6H, s, Ar-CH_3), 1.93 (6H, s, Ar-CH_3), 0.95 (2H, s, N-H), 0.38 (2H, br s, N-H); ^{1}H NMR (500 MHz, pyridine-d_5) δ 9.76 (1H, d, *J*=5 Hz, β-H), 9.53 (1H, d, *J*=5 Hz, β-H), 9.01 (1H, s, β-H), 8.59-8.55 (2H, m, β-H), 8.54-8.49 (4H, m, β-H), 8.48-8.43 (6H, m, β-H, Ar-H), 8.29 (1H, d, *J*=5 Hz, β-H), 8.24 (1H, d, *J*=5 Hz, β-H), 8.22-8.18 (4H, br s and d, *J*=8 Hz, Ar-H), 7.5-7.3 (8H, br m, Ar-H), 4.03 (3H, s, O-CH_3), 4.02 (3H, s, O-CH_3), 2.65 (3H, s, Ar-CH_3), 2.62 (6H, s, Ar-CH_3), 2.54 (3H, s, Ar-CH_3), 2.70-1.80 (12H, br s, Ar-CH_3), 2.34 (6H, s, Ar-CH_3), 2.04 (6H, s, Ar-CH_3), 1.50 (2H, s, N-H), 0.84 (2H, br s, N-H); MALDI-TOF-MS m/z calcd for $C_{92}H_{75}BrN_8O_4$ 1436.5, obsd 1436.8; UV-visible-NIR ($\lambda_{max,}$ CH_2Cl_2) 428, 502, 567, 612, 807 nm.

Figure S2. UV-visible-NIR spectra of **12** (line), **13** (dot) , and **14** (dash) in CH_2Cl_2.

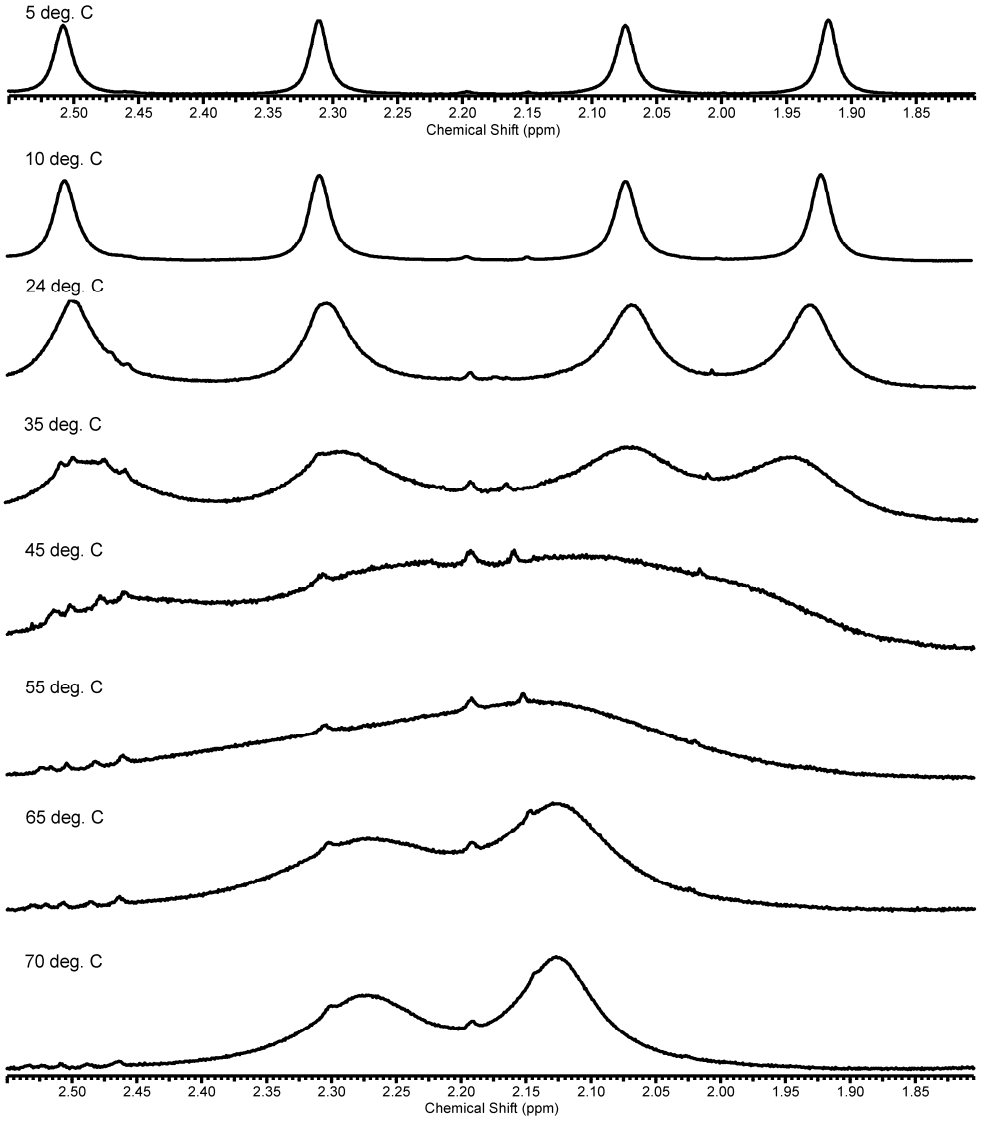


Temperature Dependent ^{1}H-NMR Spectra.

As described in the text, in the ^{1}H-NMR spectra of **13** the mesityl methyl peaks for the groups *ortho* to the macrocycle are exchange broadened at ambient temperatures, as are all the aromatic proton resonances on the peripheral rings. In addition, twice as many of these peaks were observed than expected based on C_{2h} symmetry. Two factors contribute to this phenomenon. First, the rotation of the aryl rings about their single bonds to the macrocyclic system is slow at ambient temperatures due to steric hindrance of the *ortho* substituents and the β hydrogen atoms. Secondly, the porphyrin macrocycles and the two bonds joining them do not all lie in the same plane because of steric interactions between the bromine atoms and the β-hydrogen atoms nearby on the opposite porphyrin macrocycle. This distorts the macrocyclic system from planarity to give either a C_2 or a C_i conformation in which the *ortho* methyl substituents on each mesityl ring are diastereotopic, as are the pairs of *ortho* and *meta* hydrogen atoms on all aryl rings. When the temperature of the sample was increased, the various pairs of peaks broadened further, coalesced to a single broad peak, and then sharpened to a single peak. This behavior reflects internal motions that are becoming more rapid on the NMR time scale at higher temperatures. The temperature dependence of the resonances for **13** in pyridine-d_5 solution, measured at 500 MHz, of the two constitutionally heterotopic sets of mesityl methyl protons *ortho* to the porphyrin macrocycle is shown in Figure S3 below. One set of protons has a chemical shift difference at low temperatures of 220 Hz, and coalesces to a single resonance at ca. 55 ˚C. Using the Gutowsky-Holm approximation, this yields a rate constant for the averaging process of 484 s^{-1}. From the Eyring equation, this corresponds to $\Delta G^{\ddagger}_{328}$ = 15.2 ±0.5 kcal/mol. The second set of protons shows a chemical shift difference at low temperatures of 195 Hz, and a coalescence temperature of ca. 45 ˚C. This corresponds to a rate constant of 429 s^{-1}, or $\Delta G^{\ddagger}_{318}$ = 14.8 ±0.5 kcal/mol. Averaging these values yields $\Delta G^{\ddagger}_{323}$ = 15.0 ±0.5 kcal/mol. A similar analysis for the aromatic protons *ortho* to the macrocycle of the rings bearing *p*-methoxycarbonyl groups yields $\Delta G^{\ddagger}_{297}$ = 15.7 ±0.5 kcal/mol. Because the barrier to rotation of *meso*-mesityl rings in porphyrins is >26 kcal/mol, the process that leads to averaging of the environments of the various protons is ascribed to equilibration of the distorted macrocyclic skeleton of the molecule through the planar conformation.

The ^{1}H-NMR spectra of the monobrominated compound **14** showed related broadening phenomena, but these were not investigated further.

Figure S3. Temperature dependent ^{1}H-NMR spectra for **13** in pyridine-d_5, taken at 500 MHz.



References

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