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General and Efficient Synthesis of Arylamino- and Alkylamino-Substituted Diphenylporphyrins and Tetraphenylporphyrins via Palladium-Catalyzed Multiple Amination Reactions

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A series of arylamino- and alkylamino-substituted diphenylporphyrins and tetraphenylporphyrins were efficiently synthesized by reactions of brominated porphyrin precursors with amines via palladium-catalyzed amination. The multiple amination reactions are general and suitable for a variety of amines, affording the desired aminoporphyrins in good to excellent yields. Examples include aromatic and aliphatic amines, primary and secondary amines, electron-rich, -neutral, and -poor amines as well as heteroaromatic amines and imines.

Introduction

Porphyrins and metalloporphyrins have found a broad spectrum of applications in numerous fields such as catalysis, materials and medicine.[1] It is not surprising that intense efforts have been continuously made to synthesize porphyrin derivatives with a variety of peripheral substituents. Porphyrins are generally synthesized via acid-catalyzed multiple condensations of monopyrroles or dipyrrolic intermediates with aldehydes, followed by oxidation.[2,3] Owing to the inherent unfavorable entropy associated with multiple condensation reactions along with the acidic and oxidative conditions, the classic synthesis of porphyrins typically gives low yields, requires tedious purification, and restrains efficient preparation of porphyrin derivatives with functional and sensitive groups. The new methodology introduced by Lindsey has greatly improved the reaction conditions and yields.[4,5] Recently, synthetic strategies involving the applications of transition-metal-mediated cross-coupling reactions of preformed halogenated porphyrins have proved advantageous, allowing efficient synthesis of a large number of derivatives from a single halogenated porphyrin precursor.[6] Successful examples include the applications of Suzuki[7] and Stille[8] cross-coupling reactions.

In addition to various cross-coupling reactions for carbon−carbon bond formation, the palladium-catalyzed amination of aryl halides and triflates has been emerging as a powerful approach for the formation of carbon−nitrogen bonds.[9−12] Application of palladium-catalyzed

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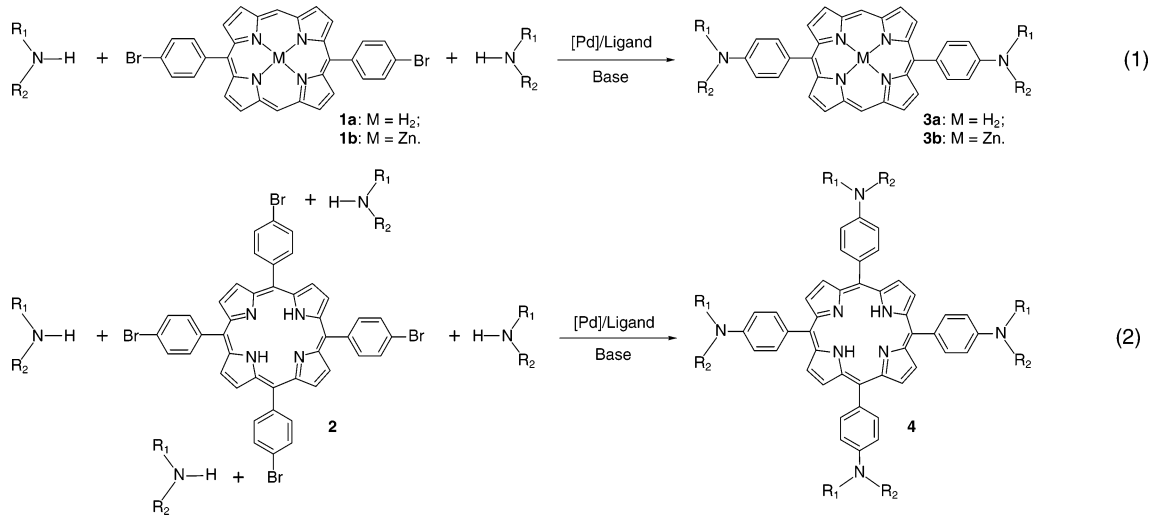
SCHEME 1. Palladium-Catalyzed Multiple Amination Reactions of Brominated Diphenylporphyrin and Tetraphenylporphyrin



amination to halogenated porphyrin precursors has not been systematically explored except a brief report by the van Lier group[13] and the work from our group.[14] We reported that *meso*-arylamino- and alkylamino-substituted porphyrins can be efficiently synthesized by reactions of *meso*-halogenated porphyrins with amines via palladium-catalyzed amination. The combination of palladium acetate and the commercially available phosphine ligand bis(2-diphenylphosphinophenyl) ether (DPEphos) is effective for catalyzing the couplings of 5-bromo-10,20-diphenylporphyrin, 5,15-dibromo-10,20-diphenylporphyrin and their zinc complexes with different amines to give the corresponding monoamino- and diamino-substituted porphyrins in high yields under mild conditions.[14] Herein, we extend our methodology to multiple-brominated diphenylporphyrins and tetraphenylporphyrins, leading to efficient and versatile synthesis of arylamino- and alkylamino-substituted porphyrin derivatives (Scheme 1). We found that DPEphos, which is highly operative for the amination of *meso*-bromoporphyrins, is ineffective for the multiple amination of bromophenylporphryrins. Through systematic studies, a different set of ligands was found to effect the transformations.

Results and Discussion

The brominated porphryin 5,15-bis(*p*-bromophenyl)-porphyrin (**1a**), its zinc complex (**1b**), and tetrakis(*p*-bromophenyl)porphyrin (**2**) were easily prepared according to the literature methods.[4,5,15,16] We first studied the double amination reactions of bromoporphyrin **1a (**Scheme 1, eq 1) that were generally carried out at 100 °C in THF for 48 h under N_2 with 1.0 equiv of **1a**, 4.0 equiv of amine, 2.5 mol % $Pd(OAc)_2$, and 5 mol % ligand in the presence of 4.0 equiv of NaO-*t*-Bu per Br at a concentration of 0.01 mmol of **1a**/1 mL of THF. To our surprise, the initial attempts to use DPEphos (**A**, Figure 1) in combination of $Pd(OAc)_2$ for double amination of bromoporphyrin **1a** with *n*-butylamine in the presence of NaO-*t*-Bu only produced a trace amount of desired product and some monoamination product along with a large amount of unreacted starting material (Table 1, entry 1). These unsuccessful results led us to systematically investigate the ligand and base effects on the double amination of bromoporphyrin **1a**. We evaluated 11 different kinds of supporting ligands including chelating diphosphines, *N*-heterocyclic carbene, and biphenyl-based electron-rich bulky monophosphines (Figure 1). In addition to DPEphos **A**, the Pd complex of ferrocene-based diphosphine **D** is also unsuitable for the reaction of bromoporphyrin **1a** with *n*-butylamine, giving no amination product (Table 1, entry 4). While improvement was observed when BINAP **C** was used (Table 1, entry 3), the best diphosphine ligand for the *n*-butylamine reaction is Xantphos **B**, which afforded the desired double amination product in 95% yield (Table 1, entry 2).

Although the monodentate *N*-heterocyclic carbene **E** is ineffective, all the biphenyl-based monophosphine ligands, in combination of $Pd(OAc)_2$, can catalyze the double amination reaction with *n*-butylamine. Among them, ligands **H** and **K** gave only the double amination product with a yield of 92% and 83%, respectively (Table 1, entries 8 and 11). While both monoamination product and unreacted starting material existed in a small amount when ligand **J** was used (Table 1, entry 10), only a trace of monoamination product was observed in the reactions with ligand **F**, **G**, and **I** (Table 1, entries 6, 7 and 9).

In addition to NaO-*t*-Bu, Cs_2CO_3 is also a viable base for the double-amination reactions of bromoporphyrin **1a**, as shown in Table 2. For the reactions with *n*-butylamine, the yields were 83% and 79% for NaO-*t*-Bu and Cs_2CO_3, respectively, when ligand **F** was employed (Table 2, entries 6 and 7). But the same reaction with the use of K_2CO_3 gave a mixture of approximately equal amounts of double-amination product, monoamination product, and unreacted starting material (Table 2, entry 8). We noticed that BINAP **C** is a much better ligand for the

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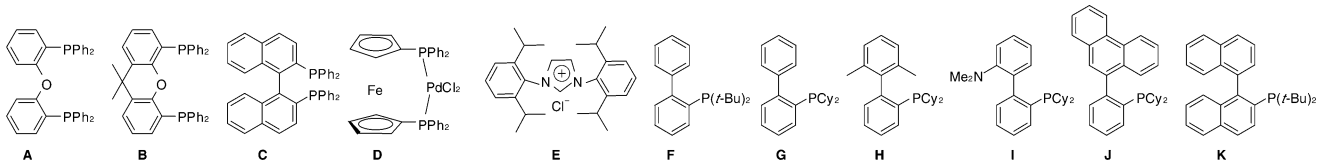


FIGURE 1. Structures of chelating diphosphine, *N*-heterocyclic carbene, and biphenyl-based electron-rich bulky monophosphine ligands.

TABLE 1. Ligand Effects on Palladium-Catalyzed Double Amination Reaction of Bromoporphyrin 1a with *n*-Butylamine[a]

entry	ligand	s.m.[b]	m.a.[b]	b.a.[b]	yield[c] (%)
1	**A**	+++	++	+	*d*
2	**B**	−	+	+++++	95
3	**C**	++	++	++	*d*
4	**D**	++++++	−	−	*d*
5	**E**	++	+++	+	*d*
6	**F**	−	++	++++	83
7	**G**	−	+	+++++	96
8	**H**	−	−	+++++	92
9	**I**	−	++	++++	85
10	**J**	+	++	+++	65
11	**K**	−	−	++++	83

[a] Reactions were carried out at 100 °C in THF for 48 h under N_2 with 1.0 equiv of **1a**, 4.0 equiv of *n*-butylamine, 2.5 mol % of $Pd(OAc)_2$, and 5 mol % ligand in the presence of 4.0 equiv of NaO-*t*-Bu per Br. Concentration: 0.01 mmol of **1a**/1 mL of THF. [b] s.m.: starting material **1a**. m.a.: monoamination product. b.a.: bisamination product. The distribution of sm, ma, and ba is estimated by TLC. [c] Yields represent isolated yields of >95% purity as determined by ^{1}H NMR. [d] No isolations were attempted.

TABLE 2. Base Effects on Palladium-Catalyzed Double Amination Reaction of Bromoporphyrin 1a[a]

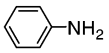
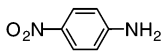
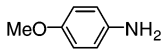
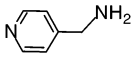
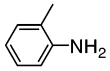
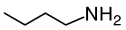
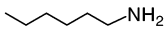
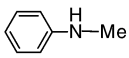
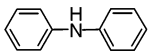
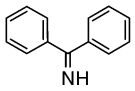
entry	amine	ligand	base	s.m.[b]	m.a.[b]	b.a.[b]	yield (%)[c]
1[e]		**C**	NaO*t*-Bu	−	+	+++++	95
2		**C**	Cs_2CO_3	−	+	+++++	92
3		**C**	K_3PO_4	+++	++	+	--[d]
4		**C**	K_2CO_3	++	++	++	--[d]
5[f]		**C**	NaO*t*-Bu	++	++	++	--[d]
6		**F**	NaO*t*-Bu	−	++	++++	83
7		**F**	Cs_2CO_3	−	++	++++	79
8		**F**	K_2CO_3	++	++	++	--[d]
9[f]		**K**	NaO*t*-Bu	−	+++	+++	69

[a] Reactions were carried out at 100 °C in THF for 48 h under N_2 with 1.0 equiv of **1a**, 4.0 equiv of *n*-butylamine, 2.5 mol % $Pd(OAc)_2$, and 5 mol % ligand in the presence of 4.0 equiv of NaO-*t*-Bu per Br. Concentration: 0.01 mmol of **1a**/1 mL of THF. [b] s.m.: starting material **1a**. m.a.: monoamination product. b.a.: bisamination product. The distribution of s.m., m.a., and b.a. is estimated by TLC. [c] Yields represent isolated yields of >95% purity as determined by ^{1}H NMR. [d] No isolations were attempted. [e] Reaction was conducted for 24 h. [f] Reaction was performed in the presence of 2.0 equiv of NaO-*t*-Bu per Br.

reaction of bromoporphyrin **1a** with aniline (Table 2, entries 1 and 2) than with *n*-butylamine (Table 1, entry 3), forming the desired double-amination product in 95% and 92% yield in the presence of NaO-*t*-Bu and Cs_2CO_3, respectively. As in the case of *n*-butylamine with ligand **F** (Table 2, entry 8), K_2CO_3 is an ineffective base for the aniline reaction (Table 2, entry 4). The same negative result was also noted when K_3PO_4 was used as a base (Table 2, entry 3). We also found the amount of base is important for the double amination reactions. When the equivalents of NaO-*t*-Bu were reduced from 4.0 to 2.0 per Br, the reaction yields were significantly decreased (Table 2, entries 5 and 9).

The above systematic studies suggested that BINAP **C** and the biphenyl-based monophosphines are effective ligands for the double amination of bromoporphyrin **1a** in the presence of either NaO-*t*-Bu or Cs_2CO_3. We subsequently used these ligands to explore the substrate scope of the reactions with different amines including aromatic and aliphatic amines, primary and secondary amines, electron-rich, -neutral, and -poor amines, as well as heteroaromatic amines and imines, as summarized in Table 3. The reaction of bromoporphyrin **1a** with aniline can be successfully catalyzed by BINAP **C** in combination of $Pd(OAc)_2$ in either THF (Table 3, entries 3−7) or in toluene (Table 3, entries 1 and 2) in the presence of either NaO-*t*-Bu (Table 3, entries 2−4 and 7) or Cs_2CO_3 (Table 3, entries 1, 5, and 6). The reaction time can be reduced from 2 days to within a day without significantly affecting the yields (Table 3, entries 3 and 4). A high yield was also achieved when the reaction temperature was dropped from 100 to 68 °C (Table 3, entry 7), though a room-temperature reaction only produced a trace of the desired product (Table 3, entry 8). Both electron-poor (Table 3, entry 9) and electron-rich (Table 3, entry 10) aniline derivatives were productively coupled with bromoporphyrin **1a**. When sterically hindered *o*-toluidine was used, the desired coupling porphyrin was obtained in 87% yield by using ligand **H** in combination of $Pd(OAc)_2$ (Table 3, entry 14). In addition to primary aniline derivatives, N-substituted secondary anilines as well as imines are suitable coupling partners with bromoporphyrin **1a**. (Table 3, entries 25−28). 4-Aminomethylpyridine, a heteroaromatic benzyl-type amine, was well coupled with bromoporphyrin **1a** to give the desired product via double amination in 88% and 80% yields by using BINAP **C** and monophosphine ligand **K**, respectively, in the presence of NaO-*t*-Bu in THF (Table 3, entries 11 and 12). A lower yield was obtained when the same reaction was performed in toluene using Cs_2CO_3 as a base (Table 3, entry 13). As indicated in Table 2, the monophosphine ligands (Figure 1) are effective ligands for the coupling reaction of aliphatic amines. We further carried out a series of reactions between bromoporphyrin **1a** and *n*-butylamine under various conditions (Table 3, entries 15−23) with different monophosphine ligands. In addition to ligand **F** (Table 3, entry 19) and **K** (Table 3, entries 15−18), monophosphine **G** (Table 3, entries 20 and 21) and **H** (Table 3, entries 22 and 23) are also competent ligands for the double amination. As demonstrated with aniline, lower reaction temperature (Table 3, entry 22) and shorter reaction time (Table 3, entries 16 and 17) were also successfully applied to the *n*-butylamine reactions. The reaction proceeded well with the use of $Pd(OAc)_2$ (Table 3, entry 22) or $Pd_2(dba)_3$ (Table 3, entry 23) as the

TABLE 3. Palladium-Catalyzed Double Amination Reactions of Bromoporphyrin 1a with Various Amines[a]

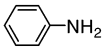
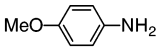
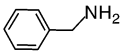
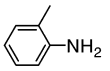
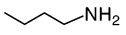
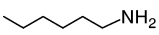
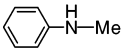
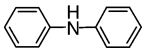
entry	amine	ligand	solvent	temp (°C)	time (h)	yield (%)[b]
1[d]		**C**	toluene	100	48	70
2		**C**	toluene	100	48	88
3		**C**	THF	100	24	95
4		**C**	THF	100	13	83
5[d]		**C**	THF	100	48	92
6[d,e]		**C**	THF	100	48	85
7		**C**	THF	68	48	92
8		**C**	THF	23	48	--[c]
9[d]		**C**	toluene	100	48	76
10		**H**	THF	100	48	93
11		**C**	THF	100	48	88
12		**K**	THF	100	48	80
13[d]		**C**	toluene	100	66	45
14		**H**	THF	100	48	87
15		**K**	THF	100	48	83
16		**K**	THF	100	24	63
17		**K**	THF	100	12	76
18[e]		**K**	THF	100	48	69
19[d]		**F**	THF	100	48	79
20[f]		**G**	THF	100	48	66
21		**G**	THF	100	48	96
22		**H**	THF	68	48	96
23[g]		**H**	THF	100	48	93
24		**H**	THF	100	48	90
25		**H**	THF	100	48	88
26		**H**	THF	100	48	81
27		**C**	THF	100	48	57
28[g]		**F**	THF	100	48	52

[a] Reactions were carried out under N_2 with 1.0 equiv of **1a**, 4.0 equiv of amine, 2.5 mol % $Pd(OAc)_2$, and 5 mol % ligand in the presence of 4.0 equiv of NaO-*t*-Bu per Br. Concentration: 0.01 mmol of **1a**/1 mL of solvent. [b] Yields represent isolated yields of >95% purity as determined by ^1H NMR. [c] Only trace amount of desired product was observed. [d] Reaction was conducted in the presence of Cs_2CO_3. [e] Reaction was performed with 2.0 equiv of amine per Br. [f] Reaction was done with 5.0 mol % $Pd(OAc)_2$ and 10 mol % ligand. [g] $Pd_2(dba)_3$ was used instead of $Pd(OAc)_2$.

palladium precursor in the presence of base NaO-*t*-Bu (Table 3, entry 21) or Cs_2CO_3 (Table 3, entry 19). Utilizing ligand **H** and $Pd(OAc)_2$, the similar reaction with *n*-hexylamine afforded the desired double-amination product in 90% yield (Table 3, entry 24).

The zinc complex of 5,15-bis(*p*-bromophenyl)porphyrin **1b** can be directly coupled with various amines to afford a series of new zinc aminoporphyrins in good to excellent yields (Table 4). For example, aniline was coupled with bromoporphyrin **1b**, using BINAP **C** and $Pd(OAc)_2$ in the presence of Cs_2CO_3, to give the desired zinc complex in 66% yield (Table 4, entry 1). Employing ligand **K** or **H** in combination of $Pd(OAc)_2$ with NaO-*t*-Bu as the base, bromoporphyrin **1b** was also successfully coupled with electron-rich aniline (Table 4, entry 2), sterically hindered aniline (Table 4, entry 4), aliphatic−aromatic secondary amine (Table 4, entry 7), and aromatic−aromatic secondary amine (Table 4, entry 8) as well as benzylamine (Table 4, entry 3). The zinc complex **1b** can also be directly coupled with aliphatic amines, suggesting the potential coordination of amines to the zinc center does not interfere with the coupling reaction. The desired aminoporphyrin zinc complexes were obtained from the reactions with *n*-butylamine (Table 4, entry 5) and *n*-hexylamine (Table 4, entry 6) by the use of ligand **K** and **B**, respectively. Assuming no difference in reactivity between *n*-butylamine and *n*-hexylamine, the monophosphine **K** appears to be a much better supporting ligand than the bisphosphine Xantphos **B** for the reaction of bromoporphyrin **1b** with aliphatic amines. The yields were 93% and 53% for ligands **K** (Table 4, entry 5) and **B** (Table 4, entry 6), respectively.

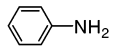
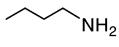
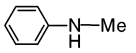
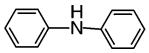
TABLE 4. Palladium-Catalyzed Double Amination Reactions of Zinc Complex of Bromoporphyrin 1b[a]

entry	amine	ligand	base	solvent	yield (%)[b]
1		**C**	Cs_2CO_3	toluene	66
2		**K**	NaO*t*-Bu	THF	68
3		**K**	NaO*t*-Bu	THF	83
4		**H**	NaO*t*-Bu	THF	73
5		**K**	NaO*t*-Bu	THF	93
6		**B**	NaO*t*-Bu	THF	53
7		**H**	NaO*t*-Bu	THF	73
8		**K**	NaO*t*-Bu	THF	57

[a] Reactions were carried out at 100 °C for 48 h under N_2 with 1.0 equiv of zinc complex of **1b**, 4.0 equiv of amine, 2.5 mol % $Pd(OAc)_2$, and 5 mol % ligand in the presence of 4.0 equiv of base per Br. Concentration: 0.01 mmol of **1b**/1 mL of solvent. [b] Yields represent isolated yields of >95% purity as determined by ^1H NMR.

The success of the double amination of bromoporphyrins **1a** and **1b** with a variety of amines prompted us to explore the possibility of one-pot quadruple amination reactions of tetrakis(*p*-bromophenyl)porphyrin (**2**) for the formation of the corresponding tetrakis(*p*-aminophenyl)-porphyrins (Scheme 1, eq 2). As shown in Table 5, excellent yields of the desired products were obtained. The combination of BINAP **C** or ligand **H** and $Pd(OAc)_2$ catalyzed the quadruple amination reactions of bromorphyrin **2** with aniline (Table 5, entry 1), *N*-methylaniline (Table 5, entry 3), and diphenylamine (Table 5, entry 4) to afford the corresponding aminoporphyrins in 91%, 82%, and 81%, respectively. It should be noted that a yield of 91% for the quadruple amination requires an average of ~98% yield for each of the four stepwise reactions. As discussed above, the monophosphine ligand **K** is an excellent ligand for the reactions with aliphatic amines. A quadruple amination of bromoporphyrin **2** with *n*-butylamine was effectively catalyzed by ligand **K** in combination of $Pd(OAc)_2$, affording the desired product with 86% yield in one pot.

TABLE 5. Palladium-Catalyzed Quadruple Amination Reactions of Bromoporphyrin 2[a]

entry	amine	[Pd]	ligand	base	yield (%)[b]
1		$Pd(OAc)_2$	**C**	NaO*t*-Bu	91
2		$Pd(OAc)_2$	**K**	NaO*t*-Bu	86
3		$Pd(OAc)_2$	**C**	NaO*t*-Bu	82
4		$Pd(OAc)_2$	**H**	NaO*t*-Bu	81

[a] Reactions were carried out at 100 °C in THF for 72 h under N_2 with 1.0 equiv of **2**, 4.0 equiv of amine, 2.5 mol % $Pd(OAc)_2$, and 5 mol % ligand in the presence of 4.0 equiv of NaO-*t*-Bu per Br. Concentration: 0.01 mmol of **2**/1 mL of THF. [b] Yields represent isolated yields of >95% purity as determined by ^{1}H NMR.

Conclusion

In summary, a series of arylamino- and alkylamino-substituted diphenylporphyrins and tetraphenylporphyrins were efficiently synthesized by reactions of easily available brominated porphyrin precursors with amines via palladium-catalyzed amination supported by suitable phosphine ligands. The one-pot multiple amination reactions are general and can be applied to a variety of amines, affording the desired aminoporphyrins in good to excellent yields. Utilizing these synthetic methods, we are currently working to construct libraries of porphyrins for potential applications in catalysis and medicine.

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere in an oven-dried Schlenk tube. Tetrahydrofuran and toluene were continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Bis(2-diphenylphosphinophenyl)ether (DPEphos, **A**), Xantphos (**B**), (±)BINAP (**C**), dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) ([(dppf)Fe]$PdCl_2$, **D**), 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride (**E**), 2-(di-*tert*-butylphosphino)biphenyl (**F**), 2-(dicyclohexylphosphino)biphenyl (**G**), 2-dicyclohexylphosphino-2′-(*N*,*N*-di-methylamino)biphenyl (**I**), and *rac*-2-(di-*tert*-butylphosphino)-1,1′-binaphthyl (**K**) were purchased from Strem Chemical Co.; 2-(dicyclohexylphosphino)-2′,6′dimethyl-biphenyl (**H**) and 2-(9-phenanthryl)phenyldicyclohexylphosphine (**J**) were synthesized by literature methods.[17−19] All ligands, palladium precursors, and bases were stored in anhydrous calcium sulfate desiccators and weighed in the air. 5,15-Bis(*p*-bromophenyl)porphyrin (**1a**) and its zinc complex (**1b**) and tetrakis(*p*-bromophenyl)porphyrin (**2**) were prepared according to the method described in the literature.[4,5,15,16]

General Procedure for Amination of Bromoporphyrin. An oven-dried Schlenk tube equipped with stirring bar was evacuated and purged with nitrogen and then charged with palladium precursor (5 mol %), phosphine ligand (10 mol %), bromophenylporphyrin (0.05 mmol), and base (4.0 equiv per Br). The tube was capped with a Teflon screwcap, evacuated, and back-filled with nitrogen. The screwcap was then replaced with a rubber septum, and solvent (2−3 mL) and amine (4.0 equiv for per Br) were added via syringe successively, followed by additional solvent (2−3 mL) to wash down possible reactants on the tube wall. The tube was purged with nitrogen (1−2 min), and the septum was then replaced by the Teflon screwcap and sealed. The reaction mixture was heated in an oil bath with stirring and monitored by TLC. After being cooled to room temperature, the reaction mixture was concentrated, dissolved in ethyl acetate, washed with water (×3), and concentrated again to dryness. The solid residue was then dissolved in a minimal amount of suitable solvent (acetone or methylene chloride or THF), and a small amount of hexanes was added to effect recrystallization. The precipitates were collected by filtration and washed with a small amount of hexanes to afford the desired product. Further purification can be carried out with flash chromatography (silica gel, methylene chloride/hexanes = 8:2−10:0).

5,15-Bis[*p*-(*N*-phenylamino)phenyl]porphyrin (Table 3, Entries 1−8). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with aniline (36.5 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **C** (6.2 mg, 0.01 mmol) in the presence of Cs_2CO_3 (130.33 mg, 0.4 mmol). The reaction was conducted in toluene at 100 °C for 48 h to afford the title compound as a dark-purple solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.29 (s, 2H), 9.39 (d, *J* = 4.5 Hz, 4H), 9.17 (d, *J* = 4.8 Hz, 4H), 8.14 (d, *J* = 8.7 Hz, 4H), 7.50 (d, *J* = 8.4 Hz, 4H), 7.38−7.46 (m, 8H), 7.06 (m, 2H), 6.13 (s, 2H), −3.05 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.9, 142.6, 135.9, 131.5, 131.0, 129.6, 121.6, 118.6, 115.7, 105.1; UV−vis ($CHCl_3$, λ_{max}, nm) 421, 508, 548, 580, 637; HRMS-EI ([M + H]$^+$) calcd for $C_{44}H_{33}N_6$, 645.2767, found 645.2734.

5,15-Bis[*p*-[*N*-(4′-nitrophenyl)amino]phenyl]porphyrin (Table 3, Entry 9). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with 4-nitroaniline (55.3 mg, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **C** (6.2 mg, 0.01 mmol) in the presence of Cs_2CO_3 (130.33 mg, 0.4 mmol). The reaction was conducted in toluene at 100 °C for 48 h to afford the title compound as a brown solid: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.64 (s, 2H), 9.82 (s, 2H), 9.67 (d, *J* = 4.2 Hz, 4H), 9.15 (d, *J* = 4.2 Hz, 4H), 8.24−8.29 (m, 8H), 7.75 (d, *J* = 7.5 Hz, 4H), 7.45 (d, *J* = 9.0 Hz, 4H), −3.19 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 150.5, 146.7, 144.7, 140.2, 138.4, 135.9, 134.9, 132.7, 130.9, 126.4, 118.9, 114.3, 105.8; UV−vis ($CHCl_3$, λ_{max}, nm) 413, 506, 542, 579, 635; HRMS-EI ([M + H]$^+$) calcd for $C_{44}H_{31}N_8O_4$ 735.2463, found 735.2436.

5,15-Bis[*p*-[*N*-(4′-methoxyphenyl)amino]phenyl]porphyrin (Table 3, Entry 10). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with *p*-anisidine (49.3 mg, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **H** (3.8 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.56 (s, 2H), 9.62 (d, *J* = 4.2 Hz, 4H), 9.15 (d, *J* = 4.8 Hz, 4H), 8.44 (s, 2H), 8.07 (d, *J* = 7.8 Hz, 4H), 7.37 (d, *J* = 9.0 Hz, 4H), 7.41 (d, *J* = 8.7 Hz, 4H), 7.02 (d, *J* = 8.4 Hz, 4H), 3.78(s, 6H), −3.09 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 154.3, 147.0, 145.2, 144.4, 136.1, 135.7, 134.7, 134.6, 132.3, 129.9, 121.4, 119.3, 114.7, 113.3, 55.3; UV−vis ($CHCl_3$, λ_{max}, nm) 418, 510, 552, 583, 640; HRMS-MALDI ([M + H]$^+$) cacld for $C_{46}H_{37}N_6O_2$ 705.2978, found 705.3018.

5,15-Bis[*p*-[*N*-(4′-methylpyridyl)amino]phenyl]porphyrin (Table 3, Entries 11−13). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with 4-aminomethylpyridine (41 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **C** (6.2 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.52 (s, 2H), 9.58 (d, *J* = 4.5 Hz, 4H), 9.07 (d, *J* = 4.2 Hz, 4H), 8.63 (d, *J* = 5.7 Hz, 4H), 7.98 (d, *J* = 8.4 Hz, 4H), 7.58 (d, *J* = 5.7 Hz, 4H), 7.05 (d, *J* = 8.7 Hz, 4H), 6.97(t, 2H), 4.61 (d, *J* = 5.7,

(17) Tomori, H.; Fox, J. M.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 5334−5341.
(18) Kaye, S.; Fox, J. M.; Hicks, F. A.; Buchwald, S. L. *Adv. Synth. Catal.* **2001**, *343*, 789−794.
(19) Yin, J. J.; Rainka, M. P.; Zhang, X. X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162−1163.

4H), −3.10 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 149.8, 148.2, 147.1, 144.6, 136.0, 134.6, 134.4, 134.3, 132.2, 130.8, 128.1, 122.5, 111.4, 105.4, 45.6; UV−vis ($CHCl_3$, λ_{max}, nm) 416, 508, 548, 581, 638; HRMS-MALDI ([M + H]$^+$) calcd for $C_{44}H_{35}N_8$ 675.2979, found 675.2973.

5,15-Bis[*p*-[*N*-(*o*-methylphenyl)amino]phenyl]porphyrin (Table 3, Entry 14). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with *o*-toluidine (43 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **H** (3.8 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.56 (s, 2H), 9.62 (d, J = 4.8 Hz, 4H), 9.16 (d, J = 4.8 Hz, 4H), 8.08 (d, J = 8.7 Hz, 4H), 7.98 (s, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.38 (d, J = 8.7 Hz, 4H), 7.27−7.38 (m, 4H), 7.04 (m, 2H), 2.44 (s, 6H), −3.10 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 147.5, 144.9, 142.6, 140.9, 135.9, 131.4, 131.2, 131.0, 128.9, 126.9, 122.6, 119.6, 115.5, 105.1, 18.0. UV−vis ($CHCl_3$, λ_{max}, nm) 419, 510, 552, 583, 640; HRMS-MALDI ([M + H]$^+$) calcd for $C_{46}H_{37}N_6$ 673.3080, found 673.3107.

5,15-Bis[*p*-(*n*-butylamino)phenyl]porphyrin (Table 3, Entries 15−23). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with *n*-butylamine (40 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **K** (3.8 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.25 (s, 2H), 9.35 (d, J = 4.6 Hz, 4H), 9.16 (d, J = 4.5 Hz, 4H), 8.06 (d, J = 8.4 Hz, 4H), 7.03 (d, J = 8.4 Hz, 4H), 3.40 (t, J = 6.9 Hz, 4H), 1.83 (m, 4H), 1.59 (m, 4H), 1.08 (m, 6H), −3.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.1, 147.8, 144.8, 136.1, 131.2, 131.1, 130.0, 119.7, 111.3, 104.9, 44.9, 31.8, 20.5, 14.1; UV−vis ($CHCl_3$, λ_{max}, nm) 419, 511, 553, 586, 641; HRMS-MALDI ([M + H]$^+$) calcd for $C_{40}H_{41}N_6$ 605.3393, found 605.3395.

5,15-Bis[*p*-(*n*-hexylamino)phenyl]porphyrin (Table 3, Entry 24). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with *n*-hexylamine (52.8 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **H** (3.78 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.25 (s, 2H), 9.35 (d, J = 4.8 Hz, 4H), 9.16 (d, J = 4.2 Hz, 4H), 8.05 (d, J = 8.4 Hz, 4H), 7.03 (d, J = 8.4 Hz, 4H), 4.05 (s, 2H), 3.40 (t, J = 7.2 Hz, 4H), 1.84 (m, 4H), 1.54 (m, 4H), 1.43 (m, 4H), 0.97 (m, 6H), −3.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.1, 147.8, 144.8, 136.1, 131.2, 131.1, 130.0, 119.7, 111.4, 104.9, 44.3, 31.8, 29.7, 27.0, 22.7, 14.1; UV−vis ($CHCl_3$, λ_{max}, nm) 421, 509, 549, 583, 638; HRMS-MALDI ([M + H]$^+$) calcd for $C_{44}H_{49}N_6$ 661.4013, found 661.3973.

5,15-Bis[*p*-(*N*-methyl-*N*-phenylamino)phenyl]porphyrin (Table 3, Entry 25). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with *N*-methylaniline (43.7 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **H** (3.78 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.28 (s, 2H), 9.39 (d, J = 4.8 Hz, 4H), 9.20 (d, J = 4.8 Hz, 4H), 8.14 (d, J = 8.7 Hz, 4H), 7.37−7.50 (m, 12H), 7.13 (dd, J = 2.1, 6.6 Hz, 2H), 3.62 (s, 6H), −3.02 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.9, 148.5, 147.6, 144.9, 135.8, 133.0, 131.4, 131.1, 129.6, 122.8, 122.7, 119.2, 116.9, 105.1, 40.6. UV−vis ($CHCl_3$, λ_{max}, nm) 413, 510, 552. 583, 640; HRMS-EI ([M] $^+$) calcd for $C_{46}H_{36}N_6$ 672.3001, found 672.3010.

5,15-Bis(*p*-diphenylaminophenyl)porphyrin (Table 3, Entries 26−27). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with diphenylamine (67.7 mg, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **H** (3.78 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.28 (s, 2H), 9.39 (d, J = 4.8 Hz, 4H), 9.20 (d, J = 4.8 Hz, 4H), 8.14 (d, J = 8.7 Hz, 4H), 7.37−7.50 (m, 12H), 7.13 (dd, J = 2.1, 6.6 Hz, 2H), 3.62 (s, 6H), −3.04 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.8, 135.8, 131.5, 131.0, 129.5, 124.9, 123.3, 121.6, 105.2; UV−vis ($CHCl_3$, λ_{max}, nm) 410, 510, 552, 583, 640; HRMS-MALDI ([M + H]$^+$) calcd for $C_{56}H_{41}N_6$ 797.3393, found 797.3398.

5,15-Bis(*p*-benzophenoneiminophenyl)porphyrin (Table 3, Entry 28). The general procedure was used to couple 5,15-bis(*p*-bromophenyl)porphyrin **1a** (31.0 mg, 0.05 mmol) with benzophenone imine (67.1 μL, 0.4 mmol), using $Pd_2(dba)_3$ (4.58 mg, 0.005 mmol) and ligand **F** (2.98 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.27 (s, 2H), 9.36 (d, J = 4.8 Hz, 4H), 9.95 (d, J = 4.8 Hz, 4H), 8.0 (d, J = 7.5 Hz, 4H), 7.95 (d, J = 8.7 Hz, 4H), 7.52 (m, 12H), 7.43 (m, 4H), 7.13 (d, J = 7.5 Hz, 4H), −3.18 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.9, 142.6, 135.9, 131.5, 131.0, 129.6, 121.6, 118.6, 115.7, 105.1; UV−vis ($CHCl_3$, λ_{max}, nm) 412, 506, 541, 578, 634; HRMS-MALDI ([M + H]$^+$) calcd for $C_{58}H_{41}N_6$ 821.3393, found 821.3370.

[5,15-Bis[*p*-(*N*-phenylamino)phenyl]porphyrinato]zinc-(II) (Table 4, Entry 1). The general procedure was used to couple the zinc complex of 5,15-bis(*p*-bromophenyl)porphyrin **1b** (34.2 mg, 0.05 mmol) with aniline (36.5 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **C** (6.2 mg, 0.01 mmol) in the presence of Cs_2CO_3 (130.33 mg, 0.4 mmol). The reaction was conducted in toluene at 100 °C for 48 h to afford the title compound as a brown solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.31 (s, 2H), 9.45 (d, J = 4.2 Hz, 4H), 9.24 (d, J = 4.5 Hz, 4H), 8.14 (d, J = 8.1 Hz, 4H), 7.50 (d, J = 8.4 Hz, 4H), 7.40−7.47 (m, 8H), 7.06 (m, 2H), 6.11 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.4, 149.3, 135.7, 132.5, 131.6, 129.5, 121.5, 118.4, 115.5, 106.1; UV−vis ($CHCl_3$, λ_{max}, nm) 419, 542, 583; HRMS-EI ([M]$^+$) calcd for $C_{44}H_{30}N_6Zn$ 706.1823, found 706.1845

[5,15-Bis[*p*-[*N*-(4′-methoxyphenyl)amino]phenyl]porphyrinato]zinc(II) (Table 4, Entry 2). The general procedure was used to couple the zinc complex of 5,15-bis-(*p*-bromophenyl)porphyrin **1b** (34.2 mg, 0.05 mmol) with *p*-anisidine (49.3 mg, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **K** (3.98 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.29 (s, 2H), 9.47 (d, J = 4.5 Hz, 4H), 9.07 (d, J = 4.2 Hz, 4H), 8.36 (s, 2H), 8.02 (d, J = 8.1 Hz, 4H), 7.39 (d, J = 8.1 Hz, 4H), 7.37 (d, J = 8.1 Hz, 4H), 7.01 (d, J = 8.1 Hz, 4H), 3.78(s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 154.1, 149.8, 148.7, 144.6, 136.1, 135.7, 134.7, 132.3, 131.9, 131.8, 121.0, 119.5, 114.7, 113.0, 105.8, 55.3; UV−vis ($CHCl_3$, λ_{max}, nm) 419, 545, 585; HRMS-MALDI ([M]$^+$) calcd for $C_{46}H_{34}N_6O_2Zn$ 766.2035, found 766.2039.

[5,15-Bis[*p*-(*N*-benzylamino)phenyl]porphyrinato]zinc-(II) (Table 4, Entry 3). The general procedure was used to couple the zinc complex of 5,15-bis(*p*-bromophenyl)porphyrin **1b** (34.2 mg, 0.05 mmol) with benzylamine (43.7 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **K** (3.98 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.17 (s, 2H), 9.35 (d, J = 4.2 Hz, 4H), 9.17 (d, J = 4.8 Hz, 4H), 8.04 (d, J = 7.2 Hz, 4H), 7.58 (d, J = 7.5 Hz, 4H), 7.35−7.49 (m, 6H), 7.02 (d, J = 7.5 Hz, 4H), 5.5 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 149.9, 148.5, 148.0, 140.4, 135.5, 131.8, 131.5, 129.9, 128.5, 127.5, 126.8, 119.9, 110.8, 105.6, 46.9; UV−vis ($CHCl_3$, λ_{max}, nm) 419, 543, 584; HRMS-MALDI ([M] $^+$) calcd for $C_{46}H_{34}N_6Zn$ 734.2136, found 734.2098

[5,15-Bis[*p*-[*N*-(*o*-methylphenyl)amino]phenyl]porphyrinato]zinc(II) (Table 4, Entry 4). The general procedure was used to couple the zinc complex of 5,15-bis(*p*-bromophenyl)porphyrin **1b** (34.2 mg, 0.05 mmol) with *o*-toluidine

(43 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **H** (3.8 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.23 (s, 2H), 9.39 (d, J = 4.8 Hz, 4H), 9.20 (d, J = 4.8 Hz, 4H), 8.11 (d, J = 8.1 Hz, 4H), 7.63 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 8.4 Hz, 4H), 7.27−7.35 (m, 4H), 7.04 (t, J = 7.8 Hz, 2H), 5.76 (s, 2H), 2.48 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.3, 149.3, 139.7, 135.8, 132.3, 131.4, 131.1, 122.2, 115.4, 105.8, 18.2; UV−vis ($CHCl_3$, λ_{max}, nm) 421, 542, 583; HRMS-MALDI ([(M − Zn) + 3H]$^+$) calcd for $C_{46}H_{37}N_6$ 673.3080, found 673.3075.

[5,15-Bis[*p*-(*n*-butylamino)phenyl]porphyrinato]zinc-(II) (Table 4, Entry 5). The general procedure was used to couple the zinc complex of 5,15-bis(*p*-bromophenyl)porphyrin **1b** (34.2 mg, 0.05 mmol) with *n*-butylamine (40 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **K** (3.98 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.26 (s, 2H), 9.44 (d, J = 4.8 Hz, 4H), 9.04 (d, J = 4.8 Hz, 4H), 7.92 (d, J = 8.1 Hz, 4H), 7.01 (d, J = 8.1 Hz, 4H), 6.04 (br, 2H), 3.28 (m, 4H), 1.76 (m, 4H), 1.55 (m, 4H), 1.05 (m, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 149.9, 148.5, 135.6, 134.5, 134.3, 131.6, 129.5, 110.4, 42.8, 31.2, 20.1, 14.0; UV−vis ($CHCl_3$, λ_{max}, nm) 419, 545, 586; HRMS-MALDI ([(M − Zn) + 3H]$^+$) calcd for $C_{40}H_{41}N_6$ 605.3393, found 605.3360.

[5,15-Bis[*p*-(*n*-hexylamino)phenyl]porphyrinato]zinc-(II) (Table 4, Entry 6). The general procedure was used to couple the zinc complex of 5,15-bis(*p*-bromophenyl)porphyrin **1b** (34.2 mg, 0.05 mmol) with *n*-hexylamine (52.8 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **B** (5.78 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.22 (s, 2H), 9.38 (d, J = 4.8 Hz, 4H), 9.18 (d, J = 4.2 Hz, 4H), 7.95 (d, J = 8.1 Hz, 4H), 6.70 (d, J = 8.1 Hz, 4H), 3.44 (m, 4H), 2.95 (m, 4H), 1.76 (m, 4H), 1.61 (m, 4H), 1.36 (m, 8H), 0.94 (m, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 150.5, 149.2, 139.4, 135.4, 132.5, 131.1, 111.4, 104.9, 44.1, 31.5, 28.0, 26.6, 22.7, 14.1; UV−vis ($CHCl_3$, λ_{max}, nm) 419, 543, 584; HRMS-MALDI ([M]$^+$) caclcd for $C_{44}H_{46}N_6Zn$ 722.3075, found 722.3100.

[5,15-Bis[*p*-(*N*-methyl-*N*-phenylamino)phenyl]porphyrinato]zinc(II) (Table 4, Entry 7). The general procedure was used to couple the zinc complex of 5,15-bis(*p*-bromophenyl)porphyrin **1b** (34.2 mg, 0.05 mmol) with *N*-methylaniline (43.7 μL, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **H** (3.78 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.24 (s, 2H), 9.39 (d, J = 4.2 Hz, 4H), 9.22 (d, J = 4.8 Hz, 4H), 8.12 (d, J = 8.1 Hz, 4H), 7.37−7.49 (m, 12H), 7.13 (m, 2H), 3.63 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.4, 149.2, 148.3, 135.6, 134.5, 132.6, 131.5, 129.5, 122.4, 122.2, 117.0, 106.0, 40.6; UV−vis ($CHCl_3$, λ_{max}, nm) 413, 544, 587; HRMS-MALDI ([(M − Zn) + 3H]$^+$) calcd for $C_{46}H_{37}N_6$ 673.3080, found 673.3104.

[5,15-Bis(*p*-diphenylaminophenyl)porphyrinato]zinc-(II) (Table 4, Entry 8). The general procedure was used to couple the zinc complex of 5,15-bis(*p*-bromophenyl)porphyrin **1b** (34.2 mg, 0.05 mmol) with diphenylamine (67.7 mg, 0.4 mmol), using $Pd(OAc)_2$ (1.12 mg, 0.005 mmol) and ligand **K** (3.98 mg, 0.01 mmol) in the presence of NaO-*t*-Bu (38.22 mg, 0.4 mmol). The reaction was conducted in THF at 100 °C for 48 h to afford the title compound: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.35 (s, 2H), 9.52 (d, J = 4.8 Hz, 4H), 9.08 (d, J = 4.5 Hz, 4H), 8.12 (d, J = 8.1 Hz, 4H), 7.37−7.51 (m, 12H), 7.17 (m, 4H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 149.4, 148.9, 147.4, 146.6, 136.6, 135.6, 132.1, 129.9, 124.5, 123.4, 121.1, 118.8, 116.7, 106.1; UV−vis ($CHCl_3$, λ_{max}, nm) 416, 543, 584; HRMS-MALDI ([(M − Zn) + 3H]$^+$) calcd for $C_{56}H_{41}N_6Zn$ 797.3393, found 797.3408.

5,10,15,20-Tetrakis[*p*-(*N*-phenylamino)phenyl]porphyrin (Table 5, Entry 1). The general procedure was used to couple 5,10,15,20-tetrakis(*p*-bromophenyl)porphyrin **2** (46.5 mg, 0.05 mmol) with aniline (73 μL, 0.8 mmol), using $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) and ligand **C** (12.4 mg, 0.02 mmol) in the presence of NaO-*t*-Bu (76.44 mg, 0.8 mmol). The reaction was conducted in THF at 100 °C for 72 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.95 (s, 8H), 8.08 (d, J = 8.1 Hz, 8H), 7.34−7.42 (m, 24H), 7.04 (t, J = 6.9 Hz, 4H), 6.05 (s, 4H), −2.66 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.9, 142.7, 135.7, 134.6, 129.5, 121.5, 119.9, 118.5, 115.3; UV−vis ($CHCl_3$, λ_{max}, nm) 433, 524, 566, 657; HRMS-MALDI ([M + H]$^+$) calcd for $C_{68}H_{51}N_8$ 979.4237, found 979.4218.

5,10,15,20-Tetrakis[*p*-(*n*-butylamino)phenyl]porphyrin (Table 5, Entry 2). The general procedure was used to couple 5,10,15,20-tetrakis(*p*-bromophenyl)porphyrin **2** (46.5 mg, 0.05 mmol) with *n*-butylamine (80 μL, 0.8 mmol), using $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) and ligand **K** (7.96 mg, 0.02 mmol) in the presence of NaO-*t*-Bu (76.44 mg, 0.8 mmol). The reaction was conducted in THF at 100 °C for 72 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.91 (s, 8H), 8.01 (d, J = 8.1 Hz, 8H), 6.95 (d, J = 8.1 Hz, 8H), 3.95 (s, 4H), 3.60 (t, J = 7.2 Hz, 8H), 1.79 (m, 8H), 1.59 (m, 8H), 1.06 (t, J = 7.2 Hz, 12H), −2.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.9, 135.8, 131.3, 120.3, 110.9, 43.9, 31.9, 20.5, 14.0; UV−vis ($CHCl_3$, λ_{max}, nm) 434, 527, 571, 661; HRMS-MALDI ([M + H]$^+$) calcd for $C_{60}H_{67}N_8$ 899.5489, found 899.5507.

5,10,15,20-Tetrakis[*p*-(*N*-methyl-*N*-phenylamino)phenyl]porphyrin (Table 5, Entry 3). The general procedure was used to couple 5,10,15,20-tetrakis(*p*-bromophenyl)porphyrin **2** (46.5 mg, 0.05 mmol) with *N*-methylaniline (87.4 μL, 0.8 mmol), using $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) and ligand **C** (12.4 mg, 0.02 mmol) in the presence of NaO-*t*-Bu (76.44 mg, 0.8 mmol). The reaction was conducted in THF at 100 °C for 72 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.78 (s, 8H), 7.92 (d, J = 7.8 Hz, 8H), 7.21−7.30 (m, 16H), 7.16 (d, J = 8.1 Hz, 8H), 7.05 (s, 2H), 6.95(t, J = 7.2 Hz, 4H), 3.42 (s, 12H), −2.81 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.9, 148.4, 135.6, 134.1, 129.5, 122.7, 122.6, 122.5, 120.1, 116.6, 116.5, 40.5; UV−vis ($CHCl_3$, λ_{max}, nm) 435, 525, 567, 657; HRMS-MALDI ([M + H]$^+$) calcd for $C_{72}H_{59}N_8$ 1035.4863, found 1035.4836.

5,10,15,20-Tetrakis[*p*-(diphenylamino)phenyl]porphyrin (Table 5, Entry 4). The general procedure was used to couple 5,10,15,20-tetrakis(*p*-bromophenyl)porphyrin **2** (46.5 mg, 0.05 mmol) with diphenylamine (135.4 mg, 0.8 mmol), using $Pd(OAc)_2$ (2.24 mg, 0.01 mmol) and ligand **H** (7.56 mg, 0.02 mmol) in the presence of NaO*t*Bu (76.44 mg, 0.8 mmol). The reaction was conducted in THF at 100 °C for 72 h to afford the title compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.02 (s, 8H), 8.12 (d, J = 8.7 Hz, 8H), 7.47 (d, J = 8.4 Hz, 8H), 7.43 (s, 16H), 7.41 (m, 4H), 7.15 (s, 8H), −2.66 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.8, 147.4, 135.9, 135.7, 129.5, 124.8, 123.3, 121.3, 119.9, 117.7; UV−vis ($CHCl_3$, λ_{max}, nm) 439, 526, 570, 659; HRMS-EI ([M + H]$^+$) calcd for $C_{92}H_{67}N_8$ 1283.5489, found 1283.5478.

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