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A General and Efficient Palladium-Catalyzed Intramolecular Cyclization Reaction of β-Brominated Porphyrins

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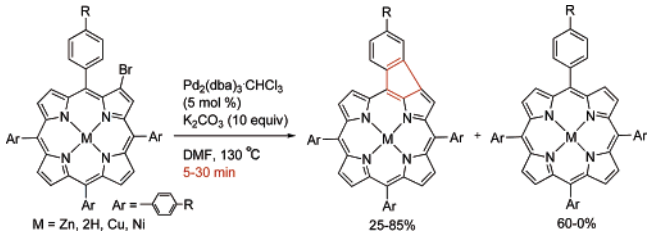

A general and efficient synthesis of fused five-membered porphyrins from the readily available β-brominated porphyrins via palladium-catalyzed intramolecular cyclization has been developed, which can be applied for various metal complexes of β-brominated porphyrins or free base ones and generally results in good yields of the fused five-membered porphyrins.

Introduction

Over the past decade interest in porphyrins with secondary ring systems fused onto the macrocyclic core has been steadily on the rise because of their bright prospects, inviting applications in various branches of optical technology and biomedicine.[1] From the structural point of view, the simplest representatives are those with newly fused five-membered rings joining the phenyl ortho-position directly to an adjacent β-position. Nevertheless, compared to other secondary ring system fused porphyrins, the chemistry of this kind of fused five-membered porphyrins has been little investigated. The main reason for this might be the lack of general and efficient synthetic methods.

Recently, a practical approach to fused five-membered porphyrin systems has emerged from the work of Boyle group.[2] Their method is based on the intramolecular Pd(0) catalyzed coupling between the *o*-iodinated *meso*-phenyl and β-position of the porphyrin. Although this method can be successfully implemented in the synthesis of the newly fused five-membered porphyrins, the preparation of the precursors themselves is rather difficult and the yields are lower. In the course of our study on porphyrin intramolecular cyclization,[3] we recently came across a useful strategy based on Zn-mediated porphyrin radicals, which enabled us to obtain a variety of the newly fused five-membered porphyrins from readily available β-brominated porphyrins.[3a] However, our method appeared to be limited because it mainly resulted in reduction products and lower yields of the desired fused five-membered ones. After many trials, we found a general and efficient palladium-catalyzed intramolecular cyclization method for formation of various fused five-membered porphyrin systems from readily available β-brominated porphyrins. Herein, the results are presented.

Results and Discussion

The zinc complex of 2-bromo-5,10,15,20-tetraphenylporphyrin **Zn1a**,[3a,4] a most readily available brominated porphyrin,[5] was employed as a model substrate for the palladium-catalyzed intramolecular cyclization reaction. The reaction was first attempted on **Zn1a** using $PdCl_2$ (10 mol %) as the source of Pd(0), K_2CO_3 (10 equiv) as base and $^nBu_4NBr$ (2.0 equiv) as additive in DMF at 130 °C.[6] After only five minutes, the color of the solution had changed from purple-red to brown-yellow. TLC of the brown-yellow solution revealed the complete loss of the starting porphyrin and the formation of two new products.

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SCHEME 1. $PdCl_2$-Catalyzed Intramolecular Cyclization Reaction of Zn1a

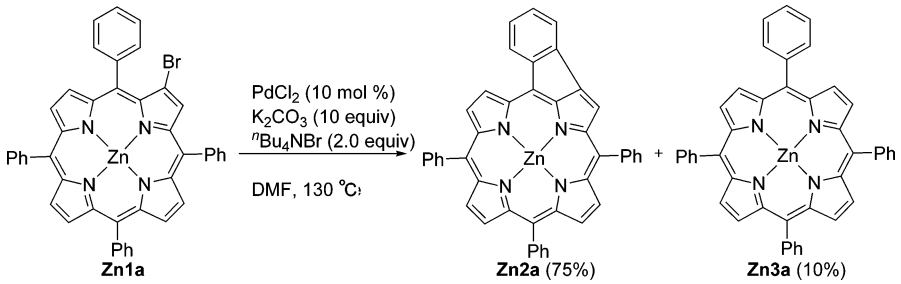
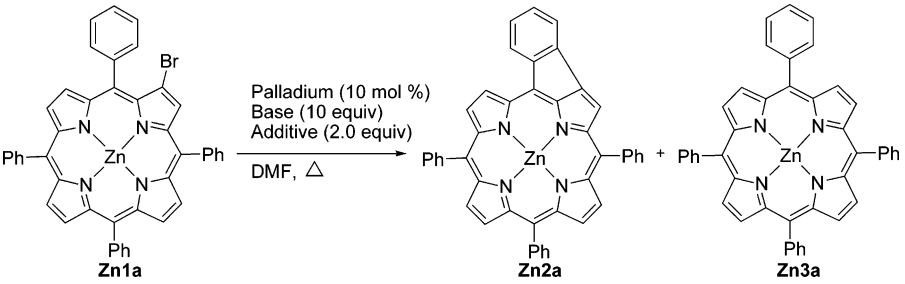


TABLE 1. The Palladium-Catalyzed Intramolecular Cyclization Reaction of Zn1a[a]



						yield (%)[b]	
entry	[Pd]	base	additive	*T* (°C)	*t* (min)	**Zn2a**	**Zn3a**
1	$PdCl_2$	K_2CO_3	$^nBu_4NBr$	130	5	75	10
2	$PdCl_2(PPh_3)_2$	K_2CO_3	$^nBu_4NBr$	130	5	70	15
3	$PdCl_2(CH_3CN)_2$	K_2CO_3	$^nBu_4NBr$	130	5	65	20
4	$PdCl_2$(dppf)[c]	K_2CO_3	$^nBu_4NBr$	130	5	80	10
5	$Pd_2(dba)_3{\cdot}CHCl_3$	K_2CO_3	$^nBu_4NBr$	130	5	85	0
6	$Pd(OAc)_2$	K_2CO_3	$^nBu_4NBr$	130	5	85	0
7	$Pd(PPh_3)_4$	K_2CO_3	$^nBu_4NBr$	130	5	50	40
8	$Pd_2(dba)_3{\cdot}CHCl_3$	K_2CO_3	LiCl	130	5	35[d]	0
9	$Pd_2(dba)_3{\cdot}CHCl_3$	K_2CO_3	*e*	130	5	85	0
10	$Pd_2(dba)_3{\cdot}CHCl_3$	NaOAc	*e*	130	5	50	35
11	$Pd_2(dba)_3{\cdot}CHCl_3$	K_3PO_4	*e*	130	5	60	25
12	$Pd_2(dba)_3{\cdot}CHCl_3$	DBU	*e*	130	5	0[f]	0
13	$Pd_2(dba)_3{\cdot}CHCl_3$	K_2CO_3	*e*	60	120	0[f]	0
14	$Pd_2(dba)_3{\cdot}CHCl_3$	K_2CO_3	*e*	100	20	78	5

[a] Reactions were carried out in DMF under N_2 with bromoporphyrin (20 mg, 1.0 equiv). Concentration: 5 mg bromoporphyrin/mL of DMF. [b] Isolated yields. [c] dppf = 1,1′-bis(diphenylphosphino)ferrocene. [d] The starting material was recovered in 55%. [e] No additive was used. [f] No conversion was observed.

Subsequent spectral analysis of them by ^1H NMR spectroscopy, mass spectrometry, and UV−vis spectra demonstrated that the main product (75%) was the desired fused five-membered porphyrin **Zn2a** and the byproduct (10%), the reduction product **Zn3a** (Scheme 1).

Encouraged with this result, we decided to optimize the reaction conditions and the results are shown in Table 1. Although the reaction proceeded smoothly in the presence of various palladium sources, Pd(II) precursors generally resulted in superior results in comparison with $Pd(PPh_3)_4$ (Table 1, entries 1−6 vs entry 7). Both $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) and $Pd(OAc)_2$ were the most suitable palladium precursors. The use of additives was unnecessary for the reaction because the reaction led to similar results in its absence and lower conversion was observed in the precence of LiCl (Table 1, entries 8 and 9). Among several common bases, K_2CO_3 as a mild base stood out (Table 1, entries 9−12). To our surprise, the organic base DBU was invalid for the reaction (Table 1, entry 12). An elevated temperature seems to be needed for effective transformation, as no conversion was observed at low temperatures even after a longer time (Table 1, entry 13). On the basis of these preliminary tests, the optimal reaction conditions were generally conducted in DMF at 130 °C under N_2 with 10 equiv of K_2CO_3 in the presence of 5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$.

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SCHEME 2. The Palladium-Catalyzed Intramolecular Cyclization Reaction of Zn4

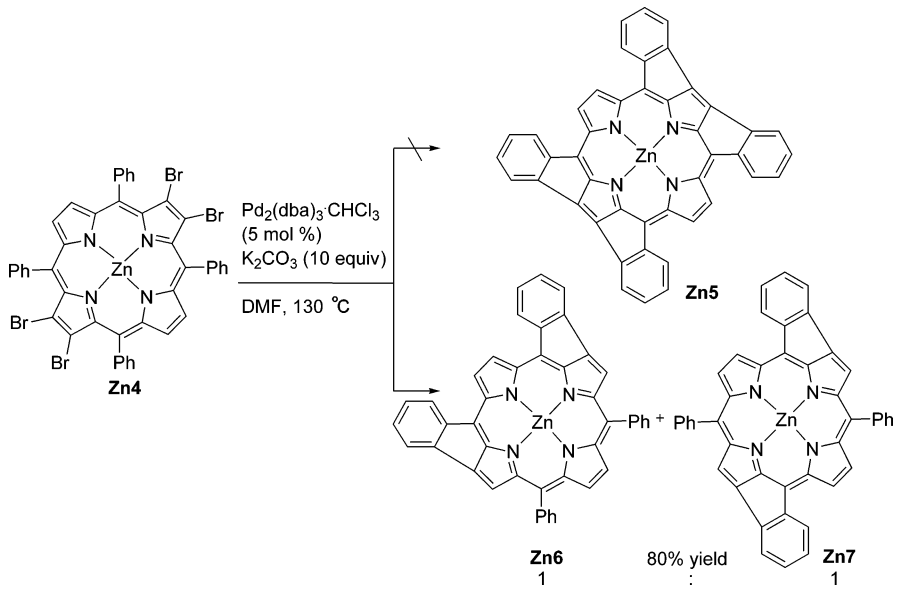
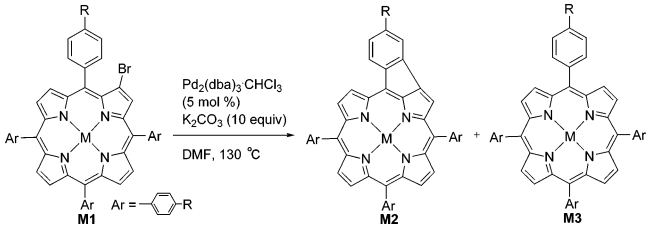


TABLE 2. The Palladium-Catalyzed Intramolecular Cyclization Reaction of Various β-Brominated Porphyrins[a]

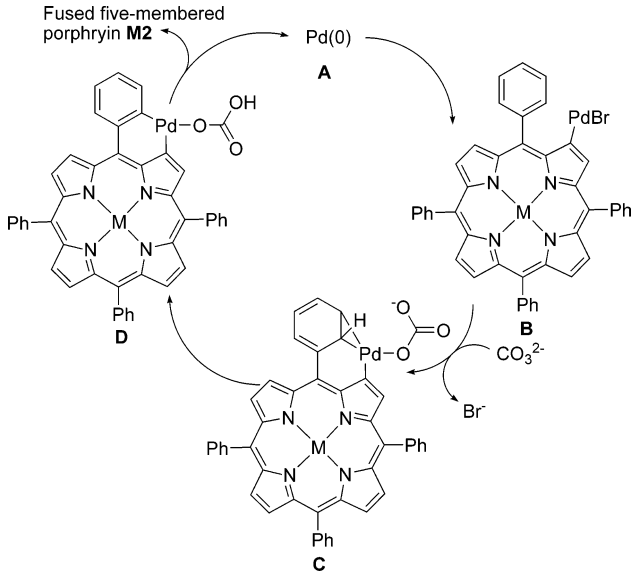


entry	M	R	reactant	*t* (min)	product (yield %)[b]	
1	Zn	H	**Zn1a**	5	**Zn2a** (85)	**Zn3a** (0)
2	Zn	Me	**Zn1b**	5	**Zn2b** (65)	**Zn3b** (0)
3	Zn	MeO	**Zn1c**	5	**Zn2c** (80)	**Zn3c** (0)
4	Zn	Cl	**Zn1d**	30	**Zn2d** (60)	**Zn3d** (25)
5	Zn	CF_3	**Zn1e**	30	**Zn2e** (55)	**Zn3e** (30)
6	Cu	H	**Cu1a**	10	**Cu2a** (62)	**Cu3a** (20)
7	Ni	H	**Ni1a**	10	**Ni2a** (25)	**Ni3a** (60)
8	2H	H	**1a**	5	**2a** (72)	**3a** (0)
9	2H	MeO	**1c**	5	**2c** (65)	**3c** (0)
10	2H	Cl	**1d**	30	**2d** (50)	**3d** (30)
11	2H	CF_3	**1e**	30	**2e** (42)	**3e** (35)

[a] Reactions were carried out at 130 °C in DMF under N_2 with bromoporphyrin (50 mg, 1.0 equiv) and K_2CO_3 (10 equiv) in the presence of $Pd_2(dba)_3$·$CHCl_3$ (5 mol %). Concentrate: 5 mg bromoporphyrin/mL of DMF. [b] Isolated yields.

Under the optimal reaction conditions, a variety of different β-brominated porphyrins could be subjected to smooth cyclization. As illustrated in Table 2, the zinc complexes of β-brominated porphyrins with an electron-donating group were effectively intramolecularly cyclizated to afford the fused five-membered porphyrins in higher yields without reduction products (Table 2, entries 2 and 3). On the contrary, for substrates with an electron-withdrawing group, yields of the desired products decreased, and the reduction products were obtained in significant yield (Table 2, entries 4 and 5). The catalytic reaction could also be applied for the copper and nickel complexes of β-brominated porphyrins, although lower yields of fused five-membered porphyrins and higher yields of reduction products were obtained (Table 2, entries 6 and 7). The potential utility of this method was further enhanced with our later discovery

SCHEME 3. Proposed Mechanism for the Palladium-Catalyzed Intramolecular Cyclization Reaction of Various β-Brominated Porphyrins



that the use of a metal ion as an "inorganic protective group" for the central −NH units was not necessary. For example, satisfactory yields of the desired fused five-membered products were achieved when reactions were carried out for the free base porphyrins **1a** and **1c** (Table 2, entries 8 and 9). Similarly, reactions utilizing **1d** and **1e** as substrates also led to acceptable yields of the products in addition to the reduction ones as expected (Table 2, entries 10 and 11).

When the zinc complex of 2,3,12,13-tetrabromotetraphenylporphyrin **Zn4** was used as a substrate under similar conditions, the double-cyclization isomers **Zn6** and **Zn7** instead of the expected highly symmetrical tetracyclization **Zn5** were also obtained in high yield (80%) (Scheme 2). By contrast, the zinc-mediated intramolecular cyclization of **Zn4** only resulted in 42% yield of the desired products.[3a] It should be mentioned that no partly reduction and cyclizated products were observed, which were the main products in the zinc-mediated intramolecular cyclization reaction of **Zn4**.[3a]

All the results may be rationalized by the mechanism similar to that which is recently proposed by Maseras et al. for the palladium-catalyzed intramolecular arylation reaction of simple aromatic halides.[7] As shown in Scheme 3, oxidative addition of active Pd(0) species **A** generated under the reaction conditions with bromoporphyrin provides porphyrin Pd(II) bromide **B**, which undergoes cyclocarbopalladation with its adjacent *meso*-phenyl ring followed by replacement of bromine ion with carbonate to form porphyrin Pd(II) complex **C**. The subsquent proton abstraction by the carbonate provides porphyrin Pd(II) complex **D**. Reductive elimination of intermediate **D** results in the formation of the desired product and the regeneration of the active species **A**, which continues the catalytic cycle.

Conclusion

In summary, a general and efficient synthesis of fused five-membered porphyrins from the readily available β-brominated porphyrins via palladium-catalyzed intramolecular cyclization has been developed. The method can be applied for various metal complexes of β-brominated porphyrins or free base ones and generally results in good yields of the fused five-membered porphyrins. In view of efficiency and convenience of the reaction and ready accessibility of the starting porphyrins, this method will permit quick entrance to various fused five-membered porphyrins which might find applications in areas such as medicine, materials, and biomimetics.

Experimental Section

General Procedure for the Palladium-Catalyzed Intramolecular Cyclization Reaction of β-Brominated Porphyrins. An oven-dried Schlenk flask was charged with porphyrin (50 mg, 1.0 equiv), K_2CO_3 (10 equiv), and $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %). The flask was then evacuated and backfilled with N_2 (three cycles). DMF (5 mg porphyrin/mL of DMF) was charged at room temperature. The resulting mixture was stirred at 130 °C for 5−30 min and then allowed to reach room temperature. CH_2Cl_2 was added, and the reaction mixture was washed with water three times. The organic layer was passed through dry silica gel and evaporated to dryness. The resulting solid was purified by flash chromatography (silica gel, 300−400 mesh, CH_2Cl_2/PE or THF/PE as eluent) to provide the desired product **M2** in good yields. An analytical sample was recrystallized from CH_2Cl_2/MeOH or THF/MeOH.

Zn2a: 85% yield. Anal. Calcd for $C_{44}H_{26}N_4Zn$: C, 78.17; H, 3.88; N, 8.29. Found: C, 77.92; H, 4.36; N, 8.10. Other analytical data are consistent with literature values.[3a]

Zn2b: 65% yield. Anal. Calcd for $C_{48}H_{34}N_4Zn{\cdot}1.5H_2O$: C, 75.93; H, 4.91; N, 7.38. Found: C, 76.11; H, 4.71; N, 6.98. Other analytical data are consistent with literature values.[3a]

Zn2c: 80% yield. Anal. Calcd for $C_{48}H_{34}N_4O_4Zn{\cdot}0.5H_2O$: C, 71.55; H, 4.44; N, 6.95. Found: C, 71.86; H, 4.64; N, 6.80. Other analytical data are consistent with literature values.[3a]

Zn2d: 60% yield. Anal. Calcd for $C_{44}H_{22}N_4Cl_4Zn{\cdot}H_2O$: C, 63.53; H, 2.91; N, 6.73. Found: C, 63.06; H, 3.23; N, 6.27. Other analytical data are consistent with literature values.[3a]

Zn2e: 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39 (s, 2H), 7.78 (d, 2H,), 7.99−8.16 (m, 12H), 8.35−8.50 (m, 5H), 8.76 (br s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −62.10 (m, 9F, CF_3), −63.78 (s, 3F, CF_3). MS (MALDI) *m*/*z*: 946.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 396 (4.7), 440 (sh, 8.4), 464 (17.8), 502 (2.4), 588 (1.0). Anal. Calcd for $C_{48}H_{22}N_4F_{12}Zn$: C, 60.24; H, 2.42; N, 5.85. Found: C, 60.64; H, 2.85; N, 5.35.

Cu2a: 62% yield. MS (MALDI) *m*/*z*: 673.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 400 (9.7), 439 (sh, 17.5), 460 (28.7), 496 (4.6), 581 (2.2), 667 (1.3), 731 (1.0). Anal. Calcd for $C_{44}H_{26}N_4Cu$: C, 78.38; H, 3.89; N, 8.31. Found: C, 78.14; H, 4.14; N, 7.93.

Ni2a: 25% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.95 (t, J = 7.5 Hz, 1H), 7.05(t, J = 7.5 Hz, 1H), 7.31−7.26 (1H, overlapping with the signal of $CHCl_3$), 7.64−7.73 (m, 13H), 7.88 (s, 1H), 7.92−7.99 (m, 8H), 8.32 (d, J = 5.1 Hz, 1H), 8.37 (d, J = 5.1 Hz, 1H), 8.62 (d, J = 4.8 Hz, 1H), 9.03 (d, J = 4.8 Hz, 1H). MS (MALDI) *m*/*z*: 668.2 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 370 (11.8), 382 (11.7), 430 (35.2), 462 (sh, 25.1), 530 (2.6), 564 (3.2), 653 (1.6), 714 (1.0). Anal. Calcd for $C_{44}H_{26}N_4Ni{\cdot}THF$: C, 77.75; H, 4.62; N, 7.56. Found: C, 78.11; H, 4.53; N, 7.44.

2a: 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: −0.22 (br s, 2H), 6.88 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.62 (s, 1H), 7.68−7.73 (m, 9H), 7.94 (d, J = 7.5 Hz, 1H), 8.02−8.08 (m, 6H), 8.24−8.38 (m, 4H), 8.60 (d, J = 5.1 Hz, 1H), 9.04 (d, J = 5.1 Hz, 1H). MS (MALDI) *m*/*z*: 613.2 (M^+ + 1). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 417 (43.6), 446 (39.6), 468 (45.6), 499 (15.6), 549 (2.2), 613 (3.0), 648 (3.2), 767 (1.0). Anal. Calcd for $C_{44}H_{28}N_4{\cdot}0.5H_2O$: C, 85.00; H, 4.72; N, 9.01. Found: C, 85.24; H, 5.09; N, 8.94.

2c: 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: −0.11 (br s, 2H), 3.88(s, 3H), 4.07−4.08 (t, 9H), 7.18−7.25 (m, 6H), 7.54−7.57 (m, 1H), 7.63 (s, 1H), 7.72−7.75 (m, 1H), 7.78−7.81 (m, 1H), 7.92−7.98 (m, 6H), 8.24−8.36 (m, 4H), 8.57 (d, J = 5.4 Hz, 1H), 8.95 (d, J = 5.4 Hz, 1H). MS (MALDI) *m*/*z*: 733.3 (M^+ + 1). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 414 (15.3), 449 (14.4), 473 (21.6), 508 (7.4), 614 (1.0), 661 (1.4). Anal. Calcd for $C_{48}H_{36}N_4{\cdot}0.5H_2O$: C, 77.71; H, 5.03; N, 7.55. Found: C, 78.01; H, 5.37; N, 7.46.

2d: 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: −0.32 (br s, 2H), 6.93−6.97 (m, 1H), 7.14 (s, 1H), 7.56 (s, 1H), 7.66−7.71 (m, 6H), 7.77 (d J = 8.7 Hz, 1H), 7.93−7.96 (m, 6H), 8.21−8.36 (m, 4H), 8.56 (d, J = 5.1 Hz, 1H), 8.95 (d, J = 5.1 Hz, 1H). MS (MALDI) *m*/*z*: 749.1 (M^+ + 1). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 421 (28.1), 445 (9.7), 468 (13.6), 501 (3.7), 549 (1.6), 585 (1.1), 642 (1.0). Anal. Calcd for $C_{44}H_{24}N_4Cl_4$: C, 70.42; H, 3.22; N, 7.47. Found: C, 70.08; H, 3.68; N, 7.23.

2e: 42% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: −0.34 (br s, 2H), 7.31−7.34 (m, 1H), 7.45 (s, 1H), 7.67 (s, 1H), 7.95−8.06 (m, 7H), 8.13−8.37 (m, 10H), 8.59 (d, J = 5.4 Hz, 1H), 9.10 (d, J = 5.4 Hz, 1H). ^{19}F (282 MHz, $CDCl_3$) δ: −63.16 (t, 9F), −64.97 (s, 3F). MS (MALDI) *m*/*z*: 885.2 (M^+ + 1). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 415 (28.9), 448 (39.6), 470 (45.0), 498 (13.6), 614 (2.6), 649 (2.9), 755 (1.0). Anal. Calcd for $C_{48}H_{24}N_4F_{12}{\cdot}0.5MeOH$: C, 64.67; H, 2.91; N, 6.22. Found: C, 65.00; H, 3.30; N, 6.22.

Zn6 + Zn7: 80% yield. MS (MALDI) *m*/*z*: 672.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 353 (2.2), 438 (6.4), 460 (28.7), 475 (4.7), 534 (3.9), 576 (1.0). Anal. Calcd for $C_{44}H_{24}N_4Zn{\cdot}1.5THF$: C, 76.77; H, 4.64; N, 7.16. Found: C, 76.40; H, 4.96; N, 7.50.

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Supporting Information Available: General methods and copies of typical ^{1}H NMR and UV−vis spectra of fused five-membered porphyrins **Zn2a**, **Ni2a**, and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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