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C−F Bond Activation by Modified Sulfinatodehalogenation: Facile Synthesis and Properties of Novel Tetrafluorobenzoporphyrins by Direct Intramolecular Cyclization and Reductive Defluorinative Aromatization of Readily Available β-Perfluoroalkylated Porphyrins

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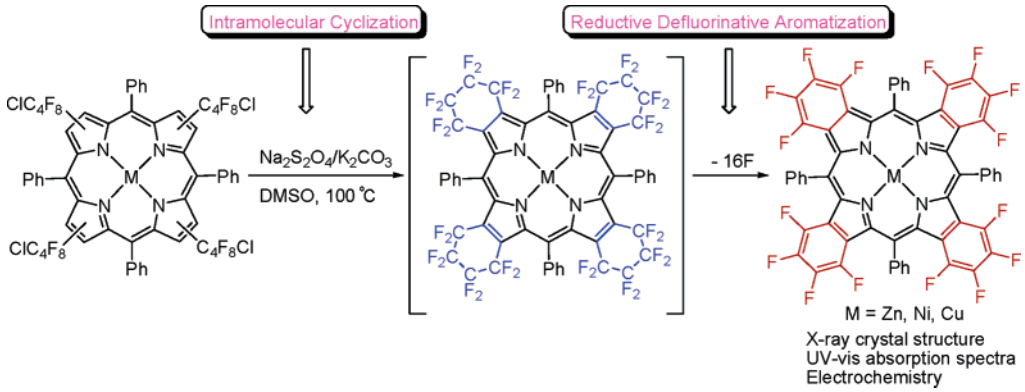

A facile and efficient synthesis of various novel fluorinated extended porphyrins has been developed. The method is based on the direct intramolecular cyclization and reductive defluorinative aromatization of readily available β-perfluoroalkylated porphyrins by highly selective C−F bond activation under modified sulfinatodehalogenation reaction conditions. Various β-(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins prepared readily by sulfinatodehalogenation reaction or palladium-catalyzed cross-coupling reaction were treated with $Na_2S_2O_4/K_2CO_3$ (10:10 equiv per R_F tail) in DMSO at 100 °C for 10−30 min, resulting in good yields of novel β-tetrafluorobenzo-*meso*-tetraphenylporphyrins. That further reduction of C−F bonds of the products was not observed under the optimal conditions indicates the high selectivity of the reaction. It was found that the amount of sodium dithionite, base, and central metal ion of substrate porphyrins play important roles in the reaction. Detailed mechanism investigations and systematic studies on X-ray crystallographic structure and photophysical and electrochemical properties of a series of new tetrafluorobenzoporphyrins are also reported.

Introduction

Activation and functionalization of C−F bonds provides a chemical challenge akin to that of C−H activation in analogous hydrocarbon compounds because fluorocarbons are noted for their chemical inertness, which is a manifestation of the great strength of the C−F bond. Although these same thermodynamic and kinetic considerations tend to disfavor C−F bond activation, numerous examples of defluorination of saturated fluorocarbons have been reported in the past decade.[1−5] However, selective reduction of perfluoroalkanes is always a challenge analogous to that of achieving alkane functionalization by selective oxidation chemistry. Recently, the use of organometallic

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complexes offers a versatile and powerful means with which to activate C−F bonds selectively.[1−5] For example, Crabtree and co-workers have made significant contributions in developing reagents and photosensitization techniques to defluorinate perfluoroalkanes using transition-metal-containing organometallic reagents.[3] Richmond's group has shown that the defluorination chemistry can be achieved utilizing early transition metallocenes and amalgamated aluminum or magnesium as the final reductant.[4] Hughes and co-workers have illustrated simple hydrogenation of a perfluorocarbon under mild conditions using various organometallic complexes.[5] However, they generally use reagents that are inconvenient and expensive. During our ongoing efforts in the synthesis and application of perfluoroalkylated porphyrins,[6] we have found unexpectedly a convenient and inexpensive intramolecular cyclization and reductive defluorinative aromatization method for the synthesis of novel fluorinated extended porphyrins directly from readily available β-perfluoroalkylated porphyrins by highly selective C−F bond activation based on a modified sulfinatodehalogenation reaction.[6d]

It is well-known that porphyrins form an important class of chromophores that are being developed and used for many different applications such as photodynamic therapy (PDT), applications in the commercial dye industry, nonlinear absorption, artificial photosynthesis, oxygen transport, and solar energy conversion.[7] Much research has been done to develop new porphyrin chromophores that display certain characteristics dependent on the application. Beginning with singlet oxygen sensitization and tumor therapy (PDT),[8] the near-infrared-absorbing porphyrinoids have wide application in many scientific fields, such as biomedical imaging and the development of nonlinear optical materials.[7] So far, there are mainly three ways to shift the absorption bands of porphyrinoids into the lower energy region, which include expanding the basic tetrapyrrolic macrocycle by adding extra pyrrolic fragments,[9] increasing the macrocycle nonplanar deformation by introducing peripheral substituents,[10] and extending the porphyrin core by fusing it with external aromatic fragments.[11] The latter approach forms a class of so-called "π-extended porphyrins", which possess interesting properties, inviting applications in various branches of optical technology and biomedicine. For example, tetrabenzoporphyrins have been found to be useful in PDT and biological oxygen imaging and have shown potential in optical limiting.[12] However, compared to regular porphyrins, the chemistry of benzoporphyrins has been little explored, mainly because of their limited synthetic availability.

In the past several years considerable progress has been made in the synthesis of *meso*-tetraarylated extended porphyrins, and some studies of their photophysical properties have been conducted. However, only a few experimental studies address the effects of nonplanarity in π-conjugated porphyrins, which can also be ascribed to their limited synthetic availability. Studies on the synthesis and properties of these molecules constitute the main focus of the present work. The extension of porphyrin pyrrole by fused benzene fragments can be achieved by three major methods: (1) a template condensation method;[9b] (2) a retro-Diels-Alder method;[13] or (3) an oxidative aromati-

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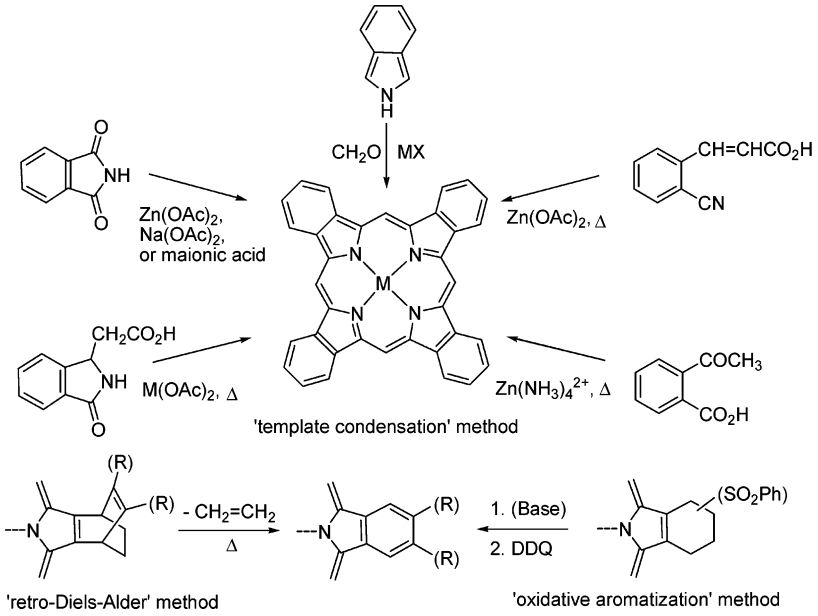
SCHEME 1. Three Major Methods for Synthesis of Benzoporphyrins



zation method[14] (Scheme 1). However, the first method is quite impractical, suffering from low yields and a large number of side products because of the extremely harsh conditions required for the macrocycle assembly (i.e., fusion at 350−400 °C). Although the latter two methods make it possible to obtain tetrabenzoporphyrins in high purity and acceptable yields, an obvious drawback is that they involve a multistep sequence.

In this paper, we present a more detailed account of the novel and appealing strategy for the synthesis of various novel tetrafluorobenzoporphyrins, which is based on the direct intramolecular cyclization and reductive defluorinative aromatization of readily available β-perfluoroalkylated porphyrins by highly selective C−F bond activation under modified sulfinatodehalogenation reaction conditions. In addition, we report the systematic X-ray crystallographic structure and photophysical and electrochemical properties of a series of novel tetrafluorobenzoporphyrins, indicating the considerable influence of fluorine atoms.

Results and Discussion

Synthesis of Various β-(ω-Chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins. For the synthesis of β-mono(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins, it was found that the sulfinatodehalogenation method was the most convenient and suitable one,[6k] although there was another method available,[6f] i.e., treatment of *meso*-tetraphenylporphyrin H_2TPP (**$H_2$1**) with perfluoroalkyl iodides R_FI (**2**) in the presence of $Na_2S_2O_4$ and $NaHCO_3$ in a solvent mixture of DMSO/CH_2Cl_2 (1:1 v/v) at 30−40 °C for several hours, that directly resulted in the corresponding β-mono(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins in acceptable yields. However, a larger excess of R_FI (50 equiv) had to be used to ensure smooth reaction. This drawback prompted us to further investigation on the reaction condition, which revealed that a smaller amount of R_FI (10 equiv) could also enable us to obtain the desired β-mono(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins in comparable yields if higher temperature and relatively longer reaction time were employed (Scheme 2).

β-Di- and β-tetra(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins were conveniently prepared by the palladium-catalyzed cross-coupling reaction of readily available bromoporphyrins with R_FI/Cu in DMSO according to our recent report[6f] (Scheme 2). It is worth mentioning that the reaction proceeded smoothly and resulted in similar yields of the desired products in the absence of the poisonous $AsPh_3$ ligand.

Intramolecular Cyclization and Reductive Defluorinative Aromatization of Various β-(ω-Chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins. With various β-(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins in hand, we initially investigated the reaction conditions in detail for the intramolecular cyclization and reductive defluorinative aromatization reaction with [β-mono(ω-chloroperfluorobutyl)-*meso*-tetraphenylporphyrinato]zinc (**Zn3b**) as model substrate. As illustrated in Table 1, on using the typical conditions of activation of the C−Cl bond of pefluoroalkyl chlorides in the modified sulfinatodehalogenation system (**Zn3b**/$Na_2S_2O_4$/$NaHCO_3$ = 1:1.5:1.5, in DMSO at 100 °C),[15] the reaction only resulted in 59% conversion of the starting material and 1.8:1 ratio of [β-monotetrafluorobenzo-*meso*-tetraphenylporphyrinato]zinc (**Zn8**) to [β-mono(octafluorocyclohexenyl)-*meso*-tetraphenylporphyrinato]zinc (**Zn9**) (Table 1, entry 1). Increase in the ratio of **Zn8** to **Zn9** was achieved by elevated amounts of $Na_2S_2O_4$/$NaHCO_3$ (Table 1, entries 2 and 3). However, too much $Na_2S_2O_4$/$NaHCO_3$ may be harmful. When 50 equiv of $Na_2S_2O_4$/$NaHCO_3$ was employed, the reaction resulted in the formation of a significant

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SCHEME 2. Synthesis of Various *β*-(*ω*-Chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins

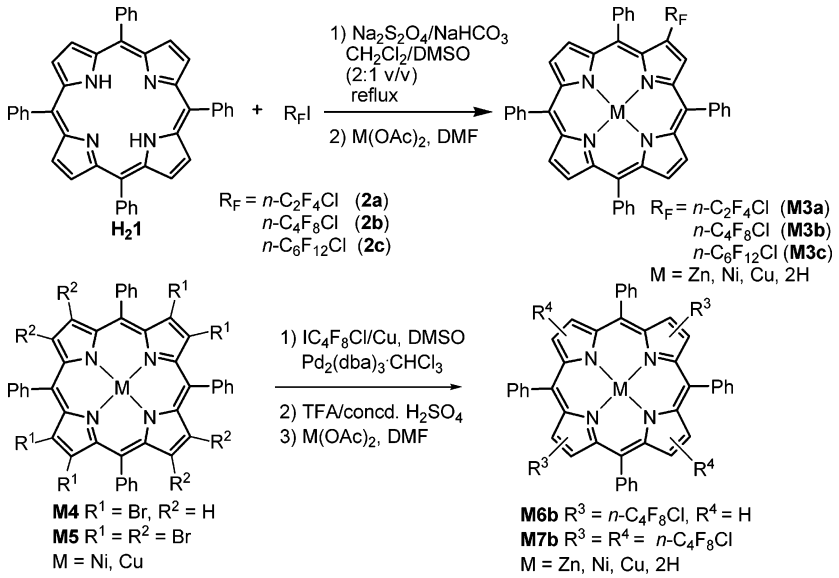
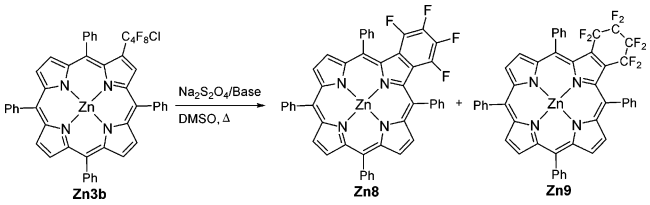


TABLE 1. Intramolecular Cyclization Aromatization of Zn3b under Various Conditions[a]



entry	$Na_2S_2O_4$ (equiv)	base (equiv)	*T* (°C)	*t* (min)	conv (%)[b]	**Zn8**/**Zn9**[b]
1	1.5	$NaHCO_3$ (1.5)	100	30	59	1.8
2	5	$NaHCO_3$ (5)	100	30	100	7.6
3	10	$NaHCO_3$ (10)	100	30	100	24.2
4	50	$NaHCO_3$ (50)	100	30	100	21.5[c]
5[d]	10	$NaHCO_3$ (10)	100	30	100	22.2[c]
6	10	K_2CO_3 (10)	100	30	100	42.9
7	10	K_2CO_3 (10)	100	10	100	12.7
8	10	KOH (10)	100	30	100	*e*
9	10	NaH (10)	100	30	100	*e*
10	10	K_2CO_3 (10)	70	30	100	6.5
11	10	K_2CO_3 (10)	25	30	0	0
12	10	*f*	100	30	100	20.2

[a] Reactions were carried out in DMSO (4 mL) under N_2 with **Zn3b** (20 mg, 1.0 equiv). [b] Determined by ^{19}F NMR. [c] A significant amount of polar side product porphyrin sulfinate salt was formed. [d] Reaction was carried out in 4 mL of DMSO/H_2O (20:1 v/v). [e] Reaction only resulted in formation of **Zn8** and no formation of **Zn9** was observed, but partial degradation of the product was observed. [f] No base was used.

amount of polar side product, which was considered as the porphyrin sulfinate salt,[15] although the conversion of **Zn3b** and ratio of **Zn8** to **Zn9** were essentially retained (Table 1, entry 4). This might be ascribed to any amount of H_2O produced from the decomposition of $NaHCO_3$ at higher temperature (100 °C) in the reaction.[15,16] Indeed, a significant amount of the polar side product porphyrin sulfinate salt was also produced when 5% (v/v) H_2O was used as a cosolvent in DMSO (Table 1, entry 5). When K_2CO_3 was used as the base, the ratio of **Zn8** to **Zn9** increased to 42.9:1 (Table 1, entry 6). In the case of stronger bases KOH and NaH, side products and partial degradation of the desired products were observed, although no **Zn9** was detected (Table 1, entries 8 and 9). In the absence of base, the reaction also proceeded smoothly and led to results similar to those for entry 3 (Table 1, entry 12). Elevated reaction temperatures facilitated the formation of **Zn8**; the ratio of **Zn8** to **Zn9** was only 6.5:1 when the reaction was carried out at 70 °C, whereas no formation of **Zn8b** and **Zn9** was observed at 25 °C (Table 1, entries10 and 11). All of these results suggested that a combination of 10 equiv of $Na_2S_2O_4$/K_2CO_3 in DMSO at 100 °C was the most effective system for the reaction. It should be pointed out that further reduction of C−F bonds of the aromatization product **Zn8** was never observed even after a longer reaction time (4 h) under the optimal conditions, indicating the high selectivity of the reaction.

Under the optimal conditions, various *β*-(*ω*-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins were effectively subjected to the intramolecular cyclization and reductive defluorinative aromatization reaction to provide novel fluorinated extended porphyrins. As summarized in Table 2, the central metal ion of the substrate porphyrins played an important role in the reaction. For example, the Zn(II) complex **Zn3b** was effectively subjected to the reaction, providing the desired product **Zn8** in excellent yield (Table 2, entry 1), whereas the reactions utilizing Ni(II) or Cu(II) porphyrin as a substrate gave relatively lower yields of the desired products (Table 2, entries 2 and 3). When the corresponding free base porphyrin **$H_2$3b** was used, the reaction resulted in 15% yield of intramolecular cyclization product **$H_2$9** in addition to 60% yield of the desired product **$H_2$8** (Table 2, entry 4). As expected, the reaction of *β*-di- and *β*-tetra(*ω*-chloroperfluorobutyl)-*meso*-tetraphenylporphyrins led to the corresponding new *β*-di- and *β*-tetra(tetrafluorobenzo)-*meso*-tetraphenylporphyrins in good yields (Table 2, entries 5−10). However, the latter turned out to be much less efficient than the former. The maximal yield achieved in the case of the latter was only 40% (Table 2, entry 8). The lower efficiency is likely to be caused by relatively poor stability of the resulting **M12**

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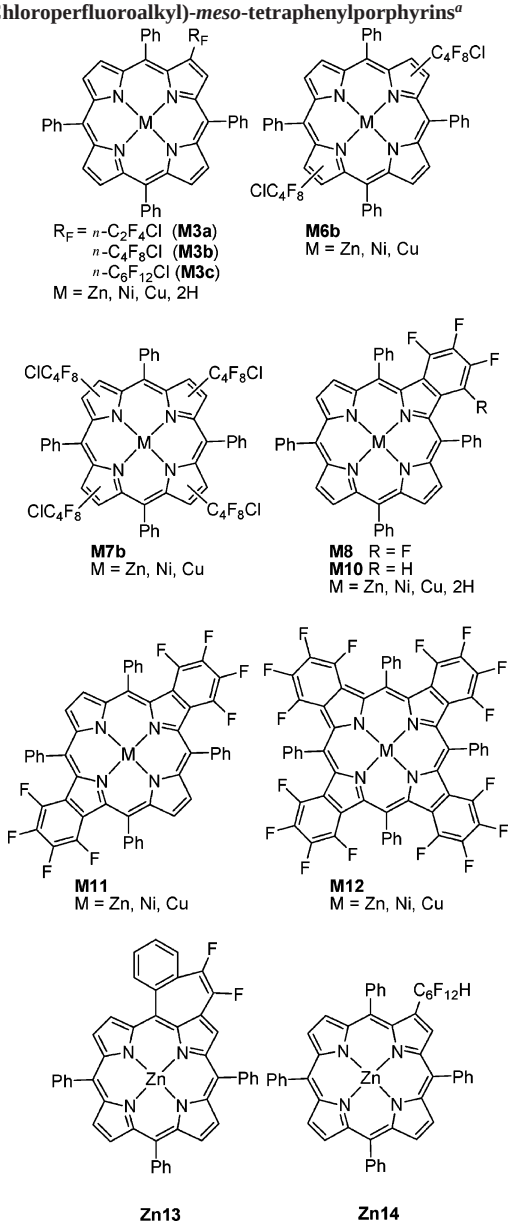
TABLE 2. Intramolecular Cyclization and Reductive Defluorinative Aromatization Reaction of Various *β*-(*ω*-Chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins[a]



entry	reactant	product	t (min)[b]	yield (%)[c]
1	**Zn3b**	**Zn8**	30	98
2	**Ni3b**	**Ni8**	30	90
3	**Cu3b**	**Cu8**	30	85
4	**$H_2$3b**	**$H_2$8**	60	60[d]
5	**Zn6b**	**Zn11**	20	95
6	**Ni6b**	**Ni11**	20	80
7	**Cu6b**	**Cu11**	20	72
8	**Zn7b**	**Zn12**	10	40[e]
9	**Ni7b**	**Ni12**	10	20[e]
10	**Cu7b**	**Cu12**	10	8[e]
11	**Zn3a**	**Zn13**	10	98
12	**Zn3c**	**Zn14**	10	52[f]

[a] Reactions were carried out in DMSO (10 mL) under N_2 with porphyrin (50 mg, 1.0 equiv) and $Na_2S_2O_4/K_2CO_3$ (10:10 equiv per R_F tail) at 100 °C. [b] Optimized reaction time. Extended reaction time did not lead to increased yield, and slow degradation of the product was observed. [c] Isolated yields. [d] Intramolecular cyclization product **$H_2$9** was also obtained in 15% yield. [e] Serious degradation of porphyrins was observed. [f] A significant amount of polar side product porphyrin sulfinate salt was formed.

(M = Zn, Ni, or Cu), which partly decompose under strongly reductive conditions. Indeed, the latter electrochemical data point to the fact that the reduction potentials of **Zn12** are lower. Longer reaction time resulted in lower yields of the desired products. In the case of **Zn3a**, the *β*-perfluoroalkyl porphyrin radical did not attack the adjacent *β*-position, but the ortho-carbon of the phenyl ring on the adjacent meso-position and subsequent reductive defluorinative aromatization provided the fluorinated fused seven-membered porphyrin **Zn13** in quantitative yield (Table 2, entry 11). When using **Zn3c** as a substrate, only H-transfer product **Zn14** was obtained and no intramolecular cyclizaiton aromatization product was observed, which was in line with the reported results (Table 2, entry 12).[17]

Mechanism Consideration. On the basis of the above experimental facts and the literature,[1,2] we propose a possible mechanism for the intramolecular cyclization and reductive defluorinative aromatization reaction. As outlined in Scheme 3, the starting porphyrin **M3b** (M = Zn, Ni, Cu, or 2H), quite similar to R_FI,[16] accepts one electron from the radical anion of sulfur dioxide, produced by decomposition of sodium dithionite, and then dissociates to give radical intermediate **A** and Cl^-. Radical adds to the *β*,*β*'-double bond of the porphyrin to form intermediate **B**, which was easily transformed into intramolecular cyclization product **M9** (M = Zn, Ni, Cu, or 2H). Electron attachment of **M9** (M = Zn, Ni, Cu, or 2H) from the radical anion of sulfur dioxide results in the formation of intermediate **C**, which accepts another electron from the radical anion of sulfur dioxide to provide intermediate **D**, and subsequent fluoride ion elimination leads to the formation of intermediate **E**. An alternative to intermediate **E** is that intermediate **C** abstracts a hydrogen atom to give intermediate **F**, which eliminates a hydrogen fluoride molecule by base to afford intermediate **E**. Repeating steps 1, 2, and 3 of intermediate **E** finally yields the desired products **M8** (M = Zn, Ni, Cu, or 2H).

This possible mechanism reasonably accounts for the fact that a greater amount of $Na_2S_2O_4$ and stronger base facilitates the formation of the desired products **M8** (M = Zn, Ni, Cu, or 2H). Furthermore, the following experiments support the above proposed mechanism: (1) **Zn9** was isolated and subjected to the reaction under similar conditions, which resulted in the formation of **Zn8** in quantitative yield. (2) When the reaction was carried out with **$H_2$3b** in the absence of base, a small amount of partial reduction product **$H_2$10** was indeed isolated, which could be rationally explained by repeating steps 1, 2, and 3 of intermediate **F**. In contrast, no formation of **$H_2$10** was observed in the presence of base, which might result from the elimination of a hydrogen fluoride molecule of intermediate **F** by the base. (3) When **$H_2$3b** was used as a substrate at relatively lower temperature (40 °C) for 8 h, partly defluorinated isomers **$H_2$15** and **$H_2$16** were obtained in 25% and 5% yield, respectively. By contrast, they were not observed in the absence of base. As is known, the C−Cl bond of perfluoroalkyl chloride cannot be activated under modified sulfinatodehalogenation reaction conditions when the reaction temperature is 40 °C.[15] The formation of **$H_2$15** and **$H_2$16** could then be reasonably explained by repeating steps 1, 4, and 5 of **$H_2$3b** directly (Scheme 4).

X-ray Crystal Structure. ORTEP views of the crystal structures for **Zn8**, **Zn11**, and **Zn12** are shown in Figure 1. Selected bond lengths and bond angles for **Zn11** and **Zn12**

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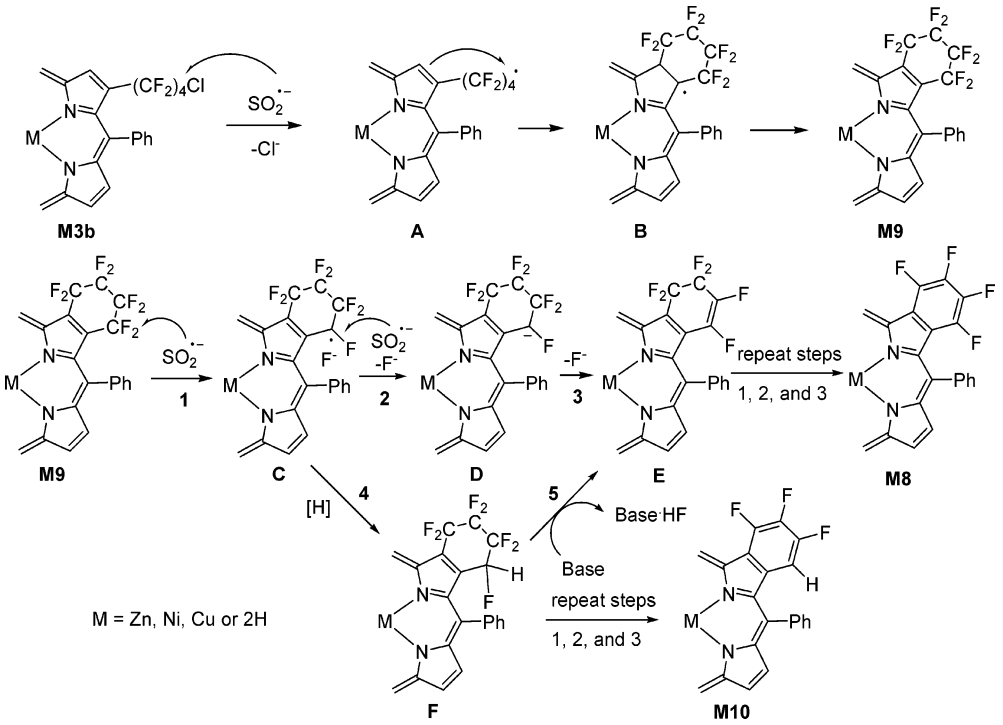
SCHEME 3. Proposed Mechanism for the Intramolecular Cyclization and Defluorinative Reductive Aromatization of Various *β*-(*ω*-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins



together with previous data for pentacoordinated ZnTPP(H_2O)[18] and **Zn8**[6d] are summarized in Table 3.

Coordination around Zn(II) in **Zn8**, **Zn11**, and **Zn12** is pentacoordinate square pyramidal, a common geometry for Zn(II) porphyrins.[19] The M−N distances are nonequivalent in different tetrafluorobenzoporphyrins because of the existence of tetrafluorobenzo groups. The Zn−N distances of the pyrrolic unit with tetrafluorobenzo groups are longer than those without tetrafluorobenzo groups, which is caused by in-plane elongation of the porphyrin core due to the steric strain and electronic effect enforced by the peripheral substituents.[19] The mechanism of elongation of the porphyrin core is partly explained by repulsion of pyrrolic $\beta-\beta$ substituents. Relief of the peripheral steric strain results in, for example, $C_\beta-C_\beta > C_\beta'-C_\beta'$ and $C_\alpha-C_m-C_{Ph} > C_\alpha'-C_m-C_{Ph}$ (Table 3). Strong electron-withdrawing substituents on the pyrrolic β-positions will decrease the electron density on its N atom, and the weakened M−N bond will be longer than the other M−N pair. Of the three structure, the difference in the Zn−N distances is larger in **Zn11** (0.096 Å) than in **Zn8** (0.086 Å), and the Zn−N distances of pyrrolic units with tetrafluorobenzo groups in **Zn8**, **Zn11**, and **Zn12** are notably longer than those of **Zn1**, as shown in Table 3.

The magnitude of distortion in the macrocycles of **Zn8**, **Zn11**, and **Zn12** is demonstrated in Figure 1. An edge-on view of the macrocycle shows clearly that the porphyrin pyrrole rings are alternately tilted up and down with respect to the least-squares plane of the 24 atoms of the porphyrin core, i.e., the macrocycle is distorted into a very nonplanar saddle conformation,[10,19,20] which presumably minimizes unfavorable contacts between meso and β substituents. The magnitude of distortion in the macrocycle rises with increasing substitution of tetrafluorobenzo groups to the pyrrole ring, indicated evidently by the fact that average displacements for the pyrrolic β-carbons from the least-squares plane for **Zn8**, **Zn11**, and **Zn12** are 0.62, 0.93 and 1.31 Å, respectively. Comparison of the root-mean-square of the sum of squares of the deviation of the 24 core atoms from their least-squares plane (Figure 1), also shows clearly the considerable distortion in these complexes, with **Zn12** being the most distorted of the three compounds.

UV−Vis Absorption Spectra. In the past, benzoporphyrins have not been easily accessible, and therefore only a few studies of their spectroscopic properties have been accomplished. No doubt, these molecules represent an interesting class of chromophores, and comprehensive photophysical assessment is yet to be done. It is known that red shifts of the ground state spectra may be attributed to some extent to saddling/ruffling of the porphyrin as well as electronic effects due to increased π-conjugation, a notion that is continuously being addressed with a range of substitutions.[21] A comparative photophysical study as well as some theoretical calculations have been recently published for Zn and Pd complexes of symmetrically extended porphyrins to assess the relative contributions of nonplanar distortion and increased π-conjugation.[21,14a−e] One of the main conclusions made was that the influence of nonplanar distortion on the red shifts of the optical transitions of laterally extended porphyrins is smaller than that of the π-conjugation. These

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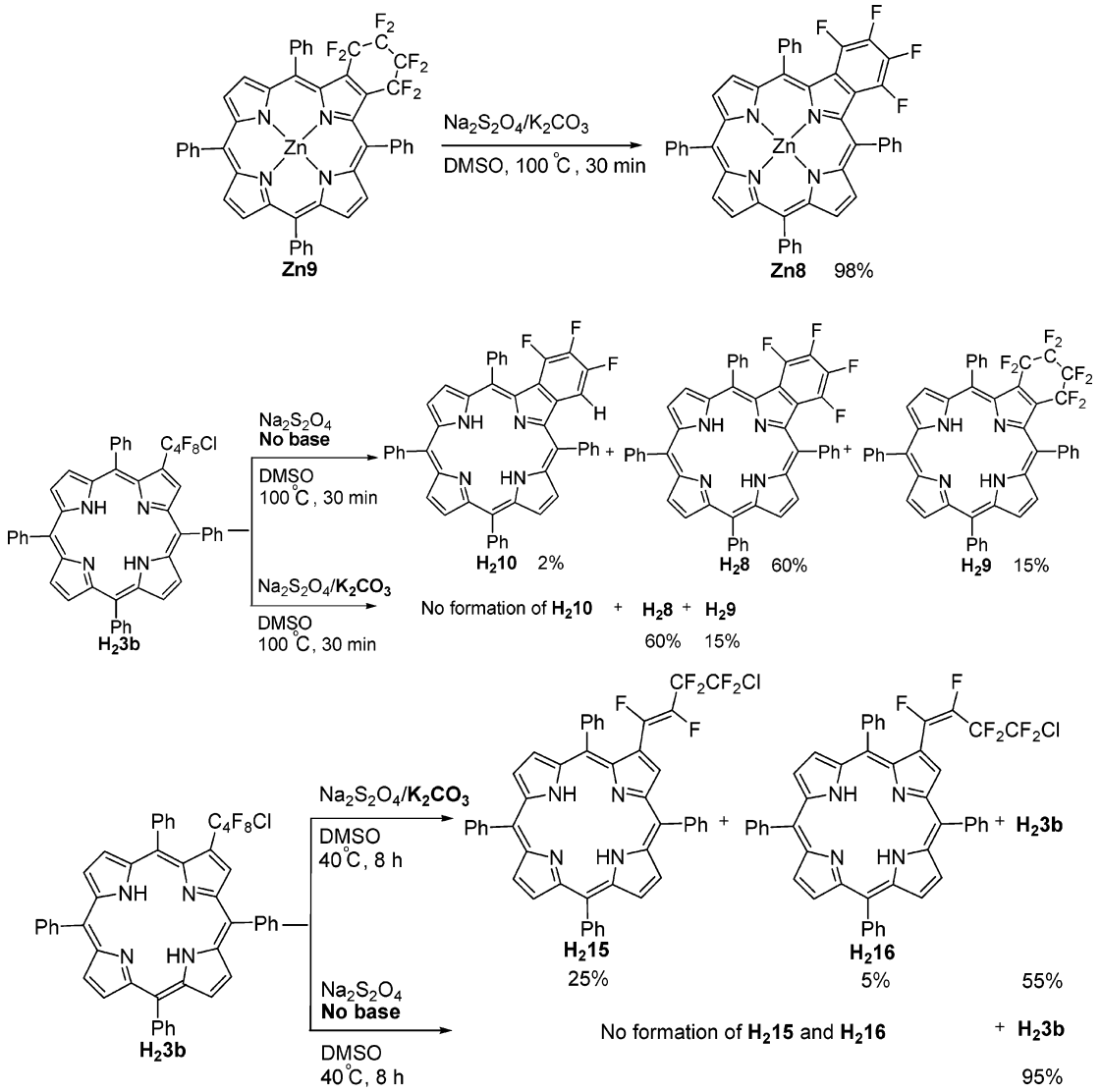
(20) (a) Medforth, C. J.; Senge, M. O.; Smith, K. M.; Sparks, L. D.; Shelnutt, J. A. *J. Am. Soc. Chem.* **1992**, *114*, 9859−9869. (b) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1−70.

(21) For recent and selective reports, see the following: (a) Rogers, J. E.; Nguyen, K. A.; Hufnagle, D. C.; McLean, D. G.; Su, W.; Gossett, K. M.; Burke, A. R.; Vinogradov, S. A.; Pachter, R.; Fleitz, P. A. *J. Phys. Chem. A* **2003**, *107*, 11331−11339. (b) Haddad, R. E.; Gazeau, S.; Pécaut, J.; Marchon, J. C.; Medforth, C. J.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 1253−1268.

SCHEME 4. Some Proofs for the Proposed Mechanism



results were mainly based on the analysis of the computationally obtained structures, since few experimental data were available. Herein we present new X-ray data and some additional photophysical measurements, further supporting the above-mentioned conclusion.

As shown in Table 4, compared to the regular *meso*-tetraphenylporphyrin, the tetrafluorobenzoporphyrins exhibit large red shifts of the absorption bands. For example, in the case of **Zn8**, **Zn11**, and **Zn12**, the shifts reach 20, 43, and 97 nm for the Soret bands, respectively. Distortion of the macrocycle of **Zn12** is similar to that of [2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphyrinato]zinc (ZnOMTPP) because they have the similar displacement for the pyrrolic β-carbons from the least-squares plane of the porphyrin core (0.93 Å for **Zn12** vs 1.05 Å for ZnOMTPP).[22a] However, the difference of the Soret band between **Zn12** and **Zn1** reaches 43 nm and that between ZnOMTPP and **Zn1** only 24 nm.[22b] This implies that the red shift of the absorption bands of laterally extended porphyrins is caused mainly by the extended π-con jugation. In addition, compared with [β-tetrabenzo-*meso*-tetraphenylporphyrinato]zinc (ZnTBTPP), **Zn12** is notably bathochromically shifted, and the difference between them reaches up to 61 nm, indicating the large influence of fluorine atoms (Table 4). These might be ascribed to the fact that the longer C−F bond length (1.4 Å compared to the C−H bond length (1.1 Å)[23] makes the tetrafluorobenzo group bulkier than the benzo group, which results in increasing macrocycle distortion in **Zn12**, although the van der Waals radius of fluorine is close to that of hydrogen.[24]

Electrochemistry. The experimental redox potentials for **Zn1**, **Zn8**, **Zn11**, and **Zn12**, determined by cyclic voltammetry, are presented in Table 5. The redox potentials of porphyrins track the energy levels of HOMOs and LUMOs of the complexes, and the differences between the first oxidation and reduction potentials, neglecting solvation effects, provide an indication of the energy of the first absorption band of porphyrins, since this transition is principally a HOMO to LUMO excitation.[25,26] The electron-withdrawing character of

(22) (a) Barkigia, K. M.; Berber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M. W.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 9675. (Erratum to document cited in CA113(24):2234155) (b) Barkigia, K. M.; Berber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M. W.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 8851−8857.

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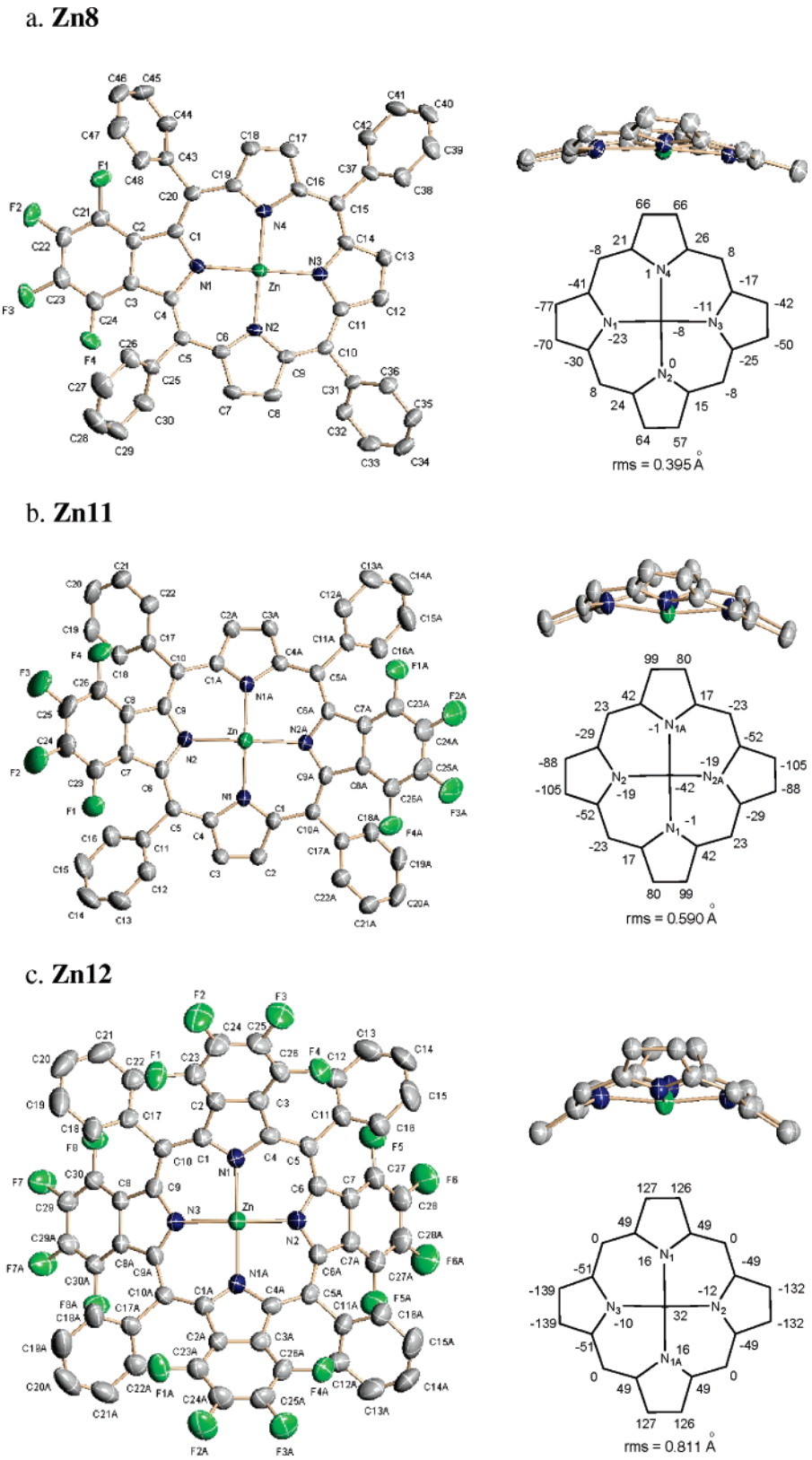
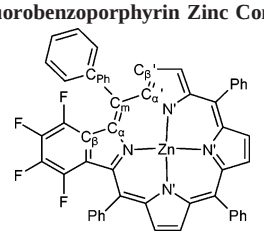


FIGURE 1. X-ray crystal structures (left column) and displacements (in 0.01 Å units) of the porphyrin core atoms from their least-squares plane of the meso carbon atoms (right column) of (a) **Zn8**, (b) **Zn11**, and (c) **Zn12**. The axial ligand, solvated molecules, and hydrogen atoms were omitted for clarity.

the tetrafluorobenzo group is expected to influence significantly the electrochemical properties of the porphyrin derivatives. Consequently, the presence of them at the periphery of the porphyrin macrocycle stabilizes both the HOMOs and the LUMOs with respect to those of the unsubstituted derivatives. Thus tetrafluorobenzoporphyrins would be easier to reduce and

TABLE 3. Selected Bond Lengths (Å), Angles (deg), and Averages for Various Tetrafluorobenzoporphyrin Zinc Complexes



	Zn8	Zn11	Zn12	Zn1
Zn−N	2.092 (3)	2.106	2.054	
Zn−N′	2.006	2.010		2.050
N−C_a	1.381 (5)	1.361	1.368	
N−C′	1.379	1.371		1.372
C_α−C_β	1.458 (5)	1.456	1.455	
C_α'−C_β'	1.430	1.437		1.442
C_β−C_β	1.401 (5)	1.419	1.413	
C_β'−C_β'	1.337	1.334		1.341
C_α−N−C_α	109.2 (3)	110.1	109.7	
C_α'−N−C_α'	106.1	106.7		106.8
N−C_α−C_β	108.4 (3)	108.4	108.3	
N′−C_α'−C_β'	109.6	109.4		
C_α−C_β−C_β	106.6 (3)	106.1	106.5	
C_α'−C_β'−C_β'	107.1	107.5		
N−C_α−C_m	122.7 (3)	122.4	122.2	
N′−C_α'−C_m	125.0	125.7		
C_α−C_m−C_{Ph}	119.9 (3)	119.5 (3)	118.6	
C_α'−C_m−C_{Ph}	114.2	115.7 (3)		
N1−Zn−N3	175.01 (13)	167.31 (15)	171.6 (2)	
N2−Zn−N4	175.20 (14)	156.05 (16)	155.9 (3)	

TABLE 4. UV−Vis Spectral Data for Various Intramolecular Cyclization Aromatic Porphyrins in CH_2Cl_2 at 25 °C

porphyrins	B bands (nm)	Q bands (nm)	
Zn1	418	547	585
Zn8	438	570	629
Zn11	461	599	670
Zn12	515	660	*a*
ZnTBTPP[b]	454	603	650
Ni1	416	520	*a*
Ni8	435	551	587
Ni11	452	572	614
Ni12	477	612	660
Cu1	415	538	*a*
Cu8	434	561	588
Cu11	456	585	628
Cu12	497	623	670

[a] Not observed. [b] ZnTBTPP = [β-tetrabenzo-*meso*-tetraphenylporphyrinato]zinc; the data come from ref 10b, p 285.

harder to oxidize. Nevertheless, this is not the case (Table 5). The differences in the reduction potentials $\Delta E_{1/2}$red(I) for **Zn1**/**Zn8**, **Zn8**/**Zn11**, and **Zn11**/**Zn12** range from +0.05 to +0.08 V, while the differences in the oxidation potentials $\Delta E_{1/2}$ox(I) for **Zn1**/**Zn8**, **Zn8**/**Zn11**, and **Zn11**/**Zn12** are negative. These data indicate that the tetrafluorobenzoporphyrins are more readily reduced and oxidized with increasing substitution of

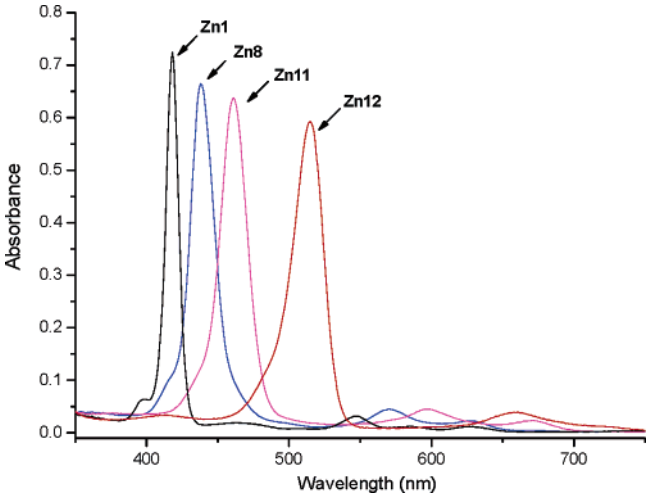


FIGURE 2. UV−vis spectra of various intramolecular cyclization aromatic porphyrin zinc complexes: (black line) **Zn1**; (blue line) **Zn8**; (pink line) **Zn11**; (red line) **Zn12**.

TABLE 5. Half-Wave Redox Potentials (V versus SCE) of Various Intramolecular Cyclization Aromatization Porphyrins in CH_2Cl_2 with 0.1 M *n*-Bu_4ClO_4 at 25 °C

porphyrins	reduction I	reduction II	$\Delta E_{1/2}$ red(I)	oxidation I	oxidation II	$\Delta E_{1/2}$ ox(I)	HOMO-LUMO	Soret λ_{max} (nm)
Zn1	−1.59	*a*		0.82	1.12		2.41	418
			+0.08			−0.03		
Zn8	−1.51	*a*		0.79	0.98		2.30	438
			+0.07			−0.03		
Zn11	−1.44	*a*		0.76	0.90		2.22	461
			+0.05			−0.19		
Zn12	−1.39	*a*		0.57	0.77		1.98	515

[a] Not observed.

tetrafluorobenzo groups. Furthermore, $E_{1/2}$ox(I) − $E_{1/2}$red(I) decreased with increasing substitution of tetrafluorobenzo groups, indicating decreasing HOMO−LUMO gaps. As a result, the strongly red-shifted Soret and Q absorption bands for them were observed (Table 5).

Redox potentials are governed not only by inductive effect but also by distortion. Electron-withdrawing substituents stabilize the LUMOs and, to a slightly lesser degree, the HOMOs. Macrocycle distortion destabilizes the HOMOs, leaving the LUMOs relatively unchanged (slight stabilization), and the destabilizing effect on the HOMOs predominates in the severely distorted porphyrins.[26] Thus, the negative values of $\Delta E_{1/2}$ox(I) for the tetrafluorobenzoporphyrin zinc complexes can be explained if the energy decrease in the HOMOs expected from substitution with additional electron-withdrawing tetrafluorobenzo groups is offset by the macrocycle saddle distortion.

Conclusions

In summary, a convenient and efficient synthesis of various novel fluorinated laterally extended porphyrins has been developed, which is based on the direct intramolecular cyclization and reductive defluorinative aromatization of readily available β-perfluoroalkylated porphyrins by highly selective C−F bond activation under modified sulfinatodehalogenation reaction conditions. This method allows us to readily obtain various potentially valuable tetrafluorobenzoporphyrins in good yields.

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(26) a) Spyroulias, G. A.; Despotopoulos, A. P.; Raptopoulou, C. P.; Terzis, A.; de Montauzon, D.; Poilblanc, R.; Coutsolelos, A. G. *Inorg. Chem.* **2002**, *41*, 2648−2659. (b) Barkigia, K. M.; Renner, M. W.; Furenlid, L. R.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1993**, *115*, 3627−3635. (c) Ochsenbein, P.; Ayougou, K.; Mandon, D.; Fischer, J.; Weiss, R.; Austin, R. N.; Jayaraj, K.; Gold, A.; Terner, J.; Fajer, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 348−350.

It is worth mentioning that further reduction of C−F bonds of the intramolecular cyclization and reductive defluorinative aromatization products are not observed under the optimal conditions, indicating the high selectivity of the reaction. Detailed studies on the reaction conditions and mechanism show that greater amounts of sodium dithionite, stronger base, and Zn(II) central ion of the substrate porphyrins facilitate the formation of the desired intramolecular cyclization and reductive defluorinative aromatization products. Subsequent systematic X-ray crystallographic structure and photophysical and electrochemical properties of a series of novel tetrafluorobenzoporphyrins indicate that the fluorine atoms impose an important influence on the porphyrins. Because of its efficiency and convenience, this method might be useful for some applications in areas such as materials, biomimetics, and medicine. Further studies on the application of this attractive reaction in the synthesis of small molecules with tetrafluorobenzo groups are now in progress.

Experimental Section

Preparation of Free Base β-Mono(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins. The improved method was adapted from a procedure reported previously for similar porphyrins.[6d,k] H_2-TPP (**$H_2$1**) (614 mg, 1.0 mmol) was dissolved in a mixture of DMSO/CH_2Cl_2 (1:2 v/v; 60 mL; solvents were not purified), and then R_FI (**2**) (10 mmol), $Na_2S_2O_4$ (2.61 g, 15 mmol), and $NaHCO_3$ (1.26 g, 15 mmol) were added in this order. The mixture was stirred at refluxing for 6−16 h under air, and the course of reaction was monitored by TLC. After cooling to room temperature, the reaction mixture was then directly poured on the top of a column of a short plug of dry silica gel. The column was eluted with CH_2Cl_2. The fractions containing product were collected and washed with water three times. The organic layer was passed though dry silica gel and concentrated to dryness. The resulting residue was purified by dry column chromatography on silica gel (300−400 mesh), using PE/CH_2Cl_2 (3:1 v/v) as eluent. The first dark-purple band was isolated and washed with CH_2Cl_2 to give the desired β-mono(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins. The products were sufficiently pure to carry through to the next reactions, and an analytical sample was recrystallized from CH_2Cl_2/MeOH.

Porphyrin $H_2$3a: 25% yield. The spectroscopic data were in agreement with previous work.[6d]

Porphyrin $H_2$3b: 30% yield. The spectroscopic data were in agreement with previous work.[6k]

Porphyrin $H_2$3c: 35% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: −2.59 (s, 2H), 7.65−7.83 (m, 12H), 8.13−8.27 (m, 8H), 8.69−8.80 (m, 4H), 8.89−8.93 (m, 2H), 9.07 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −68.27 (m, 2F), −97.58 (m, 2F), −118.23 (s, 2F), −120.46 (s, 2F). MS (ESI) *m*/*z*: 949.5 (M + H$^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 422 (82.7), 523 (3.7), 555 (1.2), 599(1.0), 656 (1.8). HRMS (MALDI): calcd for $C_{50}H_{30}N_4F_{12}$-Cl (M + H$^+$) 949.1960, found 949.19619. Anal. Calcd for $C_{50}H_{30}N_4F_{12}Cl$: C, 63.27; H, 3.08; N, 5.90. Found: C, 63.44; H, 3.46; N, 5.68.

Metalation Reaction of Various Free Base β-Mono(ω-chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins. Zn(II), Ni(II), and Cu(II) were inserted into free base porphyrins according to the procedure reported for similar porphyrins.[6b,d,e,k] Free base porphyrin **$H_2$3** (100 mg, 1.0 equiv), M(OAc)$_2$ (5.0 equiv) (M = Zn, Ni, or Cu), and DMF (10 mL) were heated at refluxing for 1−4 h. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the resulting mixture was cooled to room temperature. There were two workup methods: (1) H_2O (10 mL) was added to the mixture, and the resulting precipitated solid was filtered, washed with water and methanol, and air-dried. (2) The mixture was taken up in CH_2Cl_2, transferred to a separatory funnel, and washed with water three times. The organic layer was passed through dry silica gel and evaporated to dryness to yield the desired products. This compound was sufficiently pure for further reactions, and an analytical sample was obtained by flash column chromatography (silica gel, 300−400 mesh, PE/CH_2Cl_2 as eluent). Alternatively, Zn(II) could be inserted using CH_2Cl_2/MeOH (4:1 v/v; 10 mL) as solvent at room temperature.

Porphyrin Zn3a: 98% yield. The spectroscopic data were in agreement with previous work.[6d]

Porphyrin Zn3b: 98% yield. The spectroscopic data were in agreement with previous work.[6k]

Porphyrin Ni3b: 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51−7.72 (m, 12H), 7.82−8.00 (m, 8H), 8.59−8.70 (m, 6H), 9.08 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −68.25 (m, 2F), −96.99 (m, 2F), −116.97 (m, 2F), −119.34 (s, 2F). MS (ESI) *m*/*z*: 905.1 (M + H$^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 421 (41.0), 536 (2.6), 579 (1.0). Anal. Calcd for $C_{48}H_{27}N_4F_8ClNi\cdot 0.5H_2O$: C, 63.01; H, 3.08; N, 6.12. Found: C, 63.03; H, 3.37; N, 6.01.

Porphyrin Cu3b: 95% yield. MS (ESI) *m*/*z*: 910.2 (M + H$^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 419 (62.4), 545 (2.6), 582 (1.0). Anal. Calcd for $C_{48}H_{27}N_4F_8ClCu$: C, 63.30; H, 2.99; N, 6.15. Found: C, 63.12; H, 3.49; N 5.84.

Porphyrin Zn3c: 98% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.63−7.85 (m, 12H), 8.11−8.26 (m, 8H), 8.68 (d, J = 4.8 Hz, 1H), 8.84 (d, J = 4.8 Hz, 1H), 8.94 (d, J = 7.8 Hz, 4H), 9.34 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −68.20 (m, 2F), −96.65 (m, 2F), −117.58 (s, 2F), −120.37 (s, 2F), −121.52 (m, 4F). MS (MALDI) *m*/*z*: 1010.1 (M$^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 423 (57.7), 554 (2.2), 595 (1.0). HRMS (MALDI): calcd for $C_{50}H_{27}N_4F_{12}ClZn$ (M$^+$) 1010.1022, found 1010.10186. Anal. Calcd for $C_{50}H_{30}N_4F_{12}Cl$: C, 63.27; H, 3.08; N, 5.90. Found: C, 63.44; H, 3.46; N, 5.68.

General Procedure for Preparation of β-Di- and β-Tetra(ω-chloroperfluorobutyl)-*meso*-tetraphenylporphyrin Metal Complexes. The method was adapted from a procedure previously reported for similar porphyrins,[6f] but no poisonous $AsPh_3$ ligand was used.

Porphyrin Cu6b: 82% yield. Bromoporphyrin **Cu4** (100 mg, 0.1 mmol, 1.0 equiv), $Pd_2(dba)_3\cdot CHCl_3$ (10 mg, 10 mol %), and Cu (128 mg, 20 equiv) (Note: Copper powder used was synthesized by the reduction reaction of $CuSO_4\cdot 5H_2O$ with Zn.[6b]) were added to a Schlenk flask (50 mL). The flask was then evacuated and backfilled with nitrogen (three cycles). DMSO (20 mL) and IC_4F_8-Cl (**2b**) (363 mg, 10 equiv) were charged with a syringe at room temperature. The reaction mixture was stirred at 100 °C for 4 h and then allowed to reach room temperature. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and filtered through a short plug of dry silica gel. The solvent was washed three times with water. 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, PE as eluent) to yield the desired **Cu6b**. MS (MALDI) *m*/*z*: 1143.0 (M$^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 424 (30.4), 553 (1.0), 593 (1.0). Anal. Calcd for $C_{52}H_{26}N_4F_{16}Cl_2Cu$: C, 54.54; H, 2.29; N, 4.89. Found: C, 54.30; H, 2.21; N, 5.01.

Porphyrin Ni6b: 85% yield. This was prepared as described above for **Cu6b**. Bromoporphyrin **Ni4** (100 mg, 0.1 mmol, 1.0 equiv), $Pd_2(dba)_3\cdot CHCl_3$ (10 mg, 10 mol %), IC_4F_8Cl (**2b**) (363 mg, 10 equiv), and Cu (128 mg, 20 equiv) were used, and the reaction resulted in the desired **Ni6b** in good yield. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −68.21 (m, 4F), −98.23 (m, 4F), −117.44 (m, 4F), −119.57 (m, 4F). MS (MALDI) *m*/*z*: 1138.1 (M$^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 428 (19.5), 547 (1.0), 588 (1.0). Anal. Calcd for $C_{52}H_{26}N_4F_{16}Cl_2Ni\cdot H_2O$: C, 53.92; H, 2.44; N, 4.84. Found: C, 54.13; H, 2.38; N, 4.77.

Porphyrin Zn6b: 95% yield for two steps. This was prepared by two steps: (1) Demetallation of **Cu6b** gave free base porphyrin **$H_2$6b**. (2) Zn(II) was inserted into **$H_2$6b** to provide the desired

Zn6b. **Cu6b** (100 mg, 0.0875 mmol) was dissolved in CF_3COOH/concentrated H_2SO_4 (4:1 v/v, 5 mL) and CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 2 h, then poured carefully into ice water, and extracted with CH_2Cl_2 (15 mL). The organic layer was washed with saturated $NaHCO_3$ solution once and water twice. Then $Zn(OAc)_2 \cdot 4H_2O$ (96 mg, 5.0 equiv) and MeOH (5 mL) were added to the solution, and the resulting mixture was stirred for 1 h at room temperature. The mixture was washed with water three times, passed through dry silica gel, and evaporated to dryness to yield the desired **Zn6b**. This compound was sufficiently pure for further reactions, and an analytical sample was obtained by flash column chromatography (silica gel, 300−400 mesh, PE/CH_2Cl_2 as eluent). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −68.79 (s, 4F), −97.17 (m, 4F), −117.46 (m, 4F), −119.81 (m, 4F). MS (MALDI) *m/z*: 1144.0 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 427 (29.6), 561 (1.0), 604 (1.1). Anal. Calcd for $C_{52}H_{26}N_4F_{16}Cl_2Zn \cdot H_2O$: C, 53.61; H, 2.42; N, 4.81. Found: C, 53.65; H, 2.10; N, 4.65.

Porphyrin Cu7b: 75% yield. According to the procedure given for the preparation of **Cu6b**, bromoporphyrin **Cu5** (100 mg, 0.0765 mmol, 1.0 equiv), $Pd_2(dba)_3 \cdot CHCl_3$ (8 mg, 10 mol %), IC_4F_8Cl (**2b**) (555 mg, 20 equiv), and Cu (196 mg, 40 equiv) were used, and the reaction was carried out for 1 h, resulting in the desired **Cu7b** in good yield. MS (MALDI) *m/z*: 1611.0 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 439 (16.6), 582 (1.0), 630 (1.1). Anal. Calcd for $C_{60}H_{24}N_4F_{32}Cl_4Cu$: C, 44.64; H, 1.50; N, 3.47. Found: C, 44.40; H, 1.61; N, 3.38.

Porphyrin Ni7b: 80% yield. Similar to the procedure given for **Cu6b**, bromoporphyrin **Ni5** (100 mg, 0.0768 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (8 mg, 10 mol %), IC_4F_8Cl (**2b**) (555 mg, 20 equiv), and Cu (196 mg, 40 equiv) were used, and the reaction resulted in the desired **Ni7b** in good yield. MS (MALDI) *m/z*: 1606.0 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 443 (30.7), 559 (1.9), 603 (1.0). Anal. Calcd for $C_{60}H_{24}N_4F_{32}Cl_4Ni$: C, 44.78; H, 1.50; N, 3.48. Found: C, 44.89; H, 1.75; N, 3.32.

Porphyrin Zn7b: 95% yield for the two steps. Using the procedure described for **Zn6b**, **Cu7b** (100 mg, 0.062 mmol) was used, and the reactions afforded the desired **Zn7b** in excellent yield. MS (MALDI) *m/z*: 1612.0 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 453 (25.4), 601 (1.0), 655 (1.6). Anal. Calcd for $C_{60}H_{24}N_4F_{32}Cl_4Zn \cdot MeOH$: C, 44.46; H, 1.71; N, 3.40. Found: C, 44.58; H, 1.73; N, 2.91.

General Procedure for Intramolecular Cyclization and Reductive Defluorinative Aromatization of Various β-(ω-Chloroperfluoroalkyl)-*meso*-tetraphenylporphyrins. β-(ω-Chloroperfluoroalkyl)-*meso*-tetraphenylporphyrin (50 mg, 1.0 equiv) was dissolved in DMSO (20 mL) and heated to 100 °C, and then $Na_2S_2O_4$ (10 equiv) and K_2CO_3 (10 equiv) were added. The mixture was stirred under nitrogen for 10−30 min and cooled to room temperature, and CH_2Cl_2 (20 mL) was added. The mixture was then 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 column chromatography (silica gel, 300−400 mesh, PE/CH_2Cl_2 or PE/THF as eluent) to yield the desired products in good yields.

Porphyrin Zn8: 98% yield. The spectroscopic data were in agreement with previous work.[6d]

Porphyrin Zn9: This porphyrin was isolated as side product. The spectroscopic data were in agreement with previous work.[6d]

Porphyrin Ni8: 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69 (d, 12H), 8.00−8.23 (m, 8H), 8.52−8.60 (m, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −130.35 (d, J = 19.2 Hz, 2F), −157.05 (d, J = 18.6 Hz, 2F). MS (MALDI) *m/z*: 792.2 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 435 (26.0), 551 (1.8), 587 (1.0). Anal. Calcd for $C_{48}H_{26}N_4F_4Ni \cdot 2EtOH$: C, 70.69; H, 4.11; N, 6.34. Found: C, 70.71; H, 4.16; N, 6.34.

Porphyrin Cu8: 82% yield. MS (MALDI) *m/z*: 797.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 434 (38.5), 561 (2.5), 588 (1.0). HRMS (MALDI): calcd for $C_{48}H_{26}N_4F_4Cu$ (M^+) 797.1380, found 797.13841. Anal. Calcd for $C_{48}H_{26}N_4F_4Cu \cdot 2EtOH$: C, 70.30; H, 4.08; N, 6.31. Found: C, 70.61; H, 4.10; N, 5.98.

Porphyrin $H_2$8: 60% yield. The spectroscopic data were in agreement with previous work.[6d]

Porphyrin $H_2$9: 15% yield. The spectroscopic data were in agreement with previous work.[6d]

Porphyrin $H_2$10: 2% yield. No base was used. ^{1}H NMR (300 MHz, $CDCl_3$) δ: −2.60 (s, 2H), 6.64−6.69 (m, 1H), 7.79−7.97 (m, 12H), 8.22−8.30 (m, 8H), 8.68 (s, 2H), 8.82−8.86 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −126.14 (m, 1F), −134.43 (m, 1F), −161.78 (m, 1F). MS (MALDI) *m/z*: 719.4 ($M + H^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 429 (45.9), 478 (2.6), 523 (2.5), 601(1.0). HRMS (MALDI): calcd for $C_{48}H_{30}N_4F_3$ ($M + H^+$) 719.2388, found 719.24171.

Porphyrin Zn11: 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76−7.80 (m, 12H), 8.23−8.26 (m, 8H), 8.55 (s, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −130.57 (d, J = 19.2 Hz, 4F), −156.49 (d, J = 18.9 Hz, 4F); MS (MALDI) *m/z*: 920.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 461 (27.2), 599 (1.9), 670 (1.0). Anal. Calcd for $C_{52}H_{24}N_4F_8Zn \cdot 2H_2O$: C, 65.18; H, 2.95; N, 5.85. Found: C, 65.52; H, 2.62; N, 5.36.

Porphyrin Ni11: 80% yield. The spectroscopic data were in agreement with previous work.[6f]

Porphyrin Cu11: 72% yield. MS (MALDI) *m/z*: 919.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 456 (29.7), 585 (2.9), 628 (1.0). Anal. Calcd for $C_{52}H_{24}N_4F_8Cu \cdot 1.5H_2O$: C, 65.93; H, 2.87; N, 5.91. Found: C, 65.86; H, 2.38; N, 5.41.

Porphyrin Zn12: 40% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.81 (br s, 12H), 8.33 (br s, 8H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −131.07 (d, J = 14.1 Hz, 8F), −157.77 (d, J = 14.1 Hz, 8F). MS (MALDI) *m/z*: 1164.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 413 (1.0), 515 (17.6), 660 (1.2). HRMS (MALDI) calcd for $C_{60}H_{20}N_4F_{16}Zn$ (M^+) 1164.0719, found 1164.07184. Anal. Calcd for $C_{60}H_{20}N_4F_{16}Zn \cdot 1.5THF$: C, 62.20; H, 2.53; N, 4.55. Found: C, 62.87; H, 2.14; N, 4.55.

Porphyrin Ni12: 20% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.72 (br s, 12H), 7.96−7.98 (m, 8H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −129.42 (d, J = 16.1 Hz, 8F), −155.31 (d, J = 14.9 Hz, 8F). MS (MALDI) *m/z*: 1158.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 477 (17.7), 612 (1.0), 660 (3.4). HRMS (MALDI): calcd for $C_{60}H_{20}N_4F_{16}Ni$ (M^+) 1158.07774, found 1158.07804. Anal. Calcd for $C_{60}H_{20}N_4F_{16}Ni \cdot 0.5THF$: C, 62.29; H, 2.02; N, 4.69. Found: C, 62.50; H, 2.01; N, 4.23.

Porphyrin Cu12: 8% yield. MS (MALDI) *m/z*: 1163.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 413 (2.0), 497 (17.8), 623 (1.0), 670 (1.3). Anal. Calcd for $C_{60}H_{20}N_4F_{16}Cu \cdot 2THF$: C, 62.41; H, 2.77; N, 4.28. Found: C, 62.40; H, 2.97; N, 3.92.

Porphyrin Zn13: 98% yield. The spectroscopic data were in agreement with previous work.[6d]

Porphyrin Zn14: 52% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.02 (tt, J_1 = 52.2 Hz, J_2 = 5.4 Hz, 1H), 7.59−7.81 (m, 12H), 8.08−8.22 (m, 8H), 8.64 (d, J = 4.8 Hz, 1H), 8.80 (d, J = 4.8 Hz, 1H), 8.90 (d, J = 5.4 Hz, 4H), 9.31 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −96.59 (m, 2F), −117.66 (s, 2F), −121.56 (s, 2F), −123.96 (s, 2F), −130.09 (m, 2F), −137.44 (m, 2F). MS (MALDI) *m/z*: 976.1 (M^+). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 423 (58.8), 553 (2.3), 594 (1.0). Anal. Calcd for $C_{50}H_{28}N_4F_{12}Zn$: C, 61.39; H, 2.89; N, 5.73. Found: C, 61.70; H, 3.34; N, 5.39.

Reductive Defluorination Reaction of Free Base Porphyrin $H_2$3c. A mixture of **$H_2$3c** (100 mg, 0.118mmol, 1.0 equiv), $Na_2S_2O_4$ (205 mg, 10 equiv), and K_2CO_3 (163 mg, 10 equiv) was stirred in DMSO (20 mL) under nitrogen at 40 °C for 8 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with water three times. The organic layer was passed through dry silica gel and evaporated to dryness. The resulting solid was purified by dry column chromatography (silica gel, 300−400 mesh, PE/CH_2Cl_2, 4:1 v/v). The two dark-purple

bands were isolated and washed with CH_2Cl_2. The first band was **$H_2$16** and second **$H_2$15**.

Porphyrin $H_2$15: 25% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: −2.67 (s, 2H), 7.69−7.86 (m, 12H), 8.21−8.28 (m, 8H), 8.78 (s, 2H), 8.88−8.98 (m, 5H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −71.63 (s, 2F), −114.14 (dt, J_1 = 146 Hz, J_2 = 23.7 Hz, 1F), −115.11 (m, 2F), −160.83 (d, J = 143 Hz, 1F). MS (MALDI) *m*/*z*: 811.2 (M + H$^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 423 (78.5), 520 (3.2), 557 (1.0), 597 (1.0), 654 (1.7). Anal. Calcd for $C_{48}H_{29}N_4F_6Cl$: C, 71.07; H, 3.60; N, 6.91; F, 14.05. Found: C, 70.71; H, 3.71; N, 6.47; F, 14.05.

Porphyrin $H_2$16: 5% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: −2.72 (s, 2H), 7.77−7.80 (m, 12H), 8.21−8.23 (m, 8H), 8.78−8.99 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −70.17 (m, 2F), −88.44 (m, 1F), −114.19 (m, 2F), −149.70 (m, 1F). MS (ESI) *m*/*z*: 811.2 (M + H$^+$). UV−vis, CH_2Cl_2, λ_{max} nm (relative intensity): 422 (77.1), 520 (2.5), 554 (1.3), 596 (1.0), 652 (1.4). HRMS (ESI): calcd for $C_{48}H_{30}N_4F_6Cl$ (M + H$^+$) 811.2049710, found 811.2057703.

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Supporting Information Available: General methods, CIF files for **Zn11** and **Zn12**, and copies of typical ^{1}H and ^{19}F NMR spectra of porphyrins **Zn3a**, **Zn3b**, **Zn3c**, **Zn8**, **Zn9**, **$H_2$8**, **$H_2$9**, **$H_2$10**, **Zn11**, **Zn12**, **Zn13**, **Zn14**, **$H_2$15**, and **$H_2$16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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