Unexpected Intramolecular Cyclization of 2-(Perfluoroalkyl)tetraarylporphyrin Radicals: Approaches for the Intramolecular Cyclization of 2-(Perfluoroalkyl)tetraarylporphyrin Radicals

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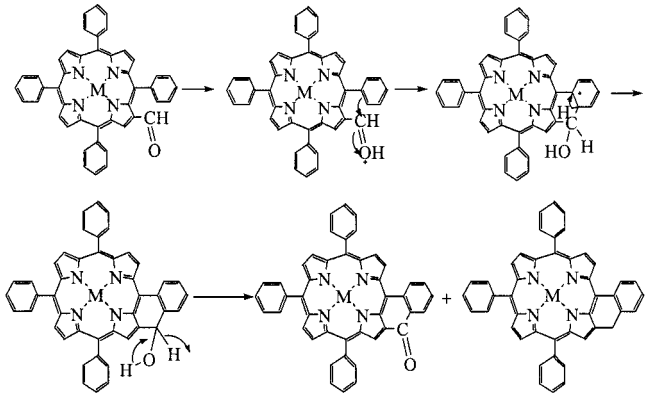
β-(Perfluoroalkyl)tetraarylporphyrin radicals, generated by the reaction of $I(CF_2)_nX$ (n = 2–5; X = I, Cl) with porphyrins in the presence of $Na_2S_2O_4/NaHCO_3$ in $DMSO/CH_2Cl_2$ or DMSO, undergo cyclizations at the *ortho* position of a neighbouring phenyl ring and/or adjacent pyrrolic unit to give five-, six-, seven-, and eight-membered fused porphyrins.

Introduction

The most widely used models for natural porphyrins are the *meso*-tetraarylporphyrins[1] because they can be easily prepared, usually in a single step, and, due to their inertness, their aryl substituents do not interfere with reactions performed at other sites, such as the pyrrolic position or the central metal. Substitutions at the pyrrolic β-position of simple tetraarylporphyrins are usually used for side-chain extension,[2] redox-potential variation,[3] N−H tautomerism, etc.[4] whilst maintaining the phenyl rings of the macrocycles intact. However, to the best of our knowledge, there are two exceptions: intramolecular cyclizations of the pyrrolic unit and an *ortho* position of the vicinal phenyl moiety occur in two different ways.

The demetalation of Cu and Ni complexes of β-formyl-*meso*-tetraphenylporphyrins in strong acid, which results in the formation of naphthoporphyrin derivatives containing an additional fused ring, was the first example of these unusual cationic intramolecular cyclizations.[5] The first step of the cyclization of β-formyl-*meso*-tetraarylporphyrins can be seen as an electrophilic attack of the protonated carbonyl carbon on the vicinal phenyl group. The resulting alcohol undergoes protonation and loss of water to yield a stable, delocalized carbocation, which disportionates by intermolecular hydride transfer to give the cyclized ketones and the reduced products (Scheme 1).



Scheme 1

Another exception is the Bergman cyclization of (2,3-diethynyl-5,10,15,20-tetraphenylporphyrin)Ni^{II} under ambient conditions in the presence of DDQ. A 1,4-didehydrobenzene diradical is proposed to be the intermediate, which then undergoes a tandem radical cyclization with the neighboring *meso*-phenyl substituents, followed by dehydrogenation, to afford highly conjugated macrocycles, picenoporphyrins (Scheme 2).[6]

We describe here a novel intramolecular cyclization of β-(perfluoroalkyl)porphyrin radicals at the *ortho* position of a neighbouring phenyl moiety as well as an adjacent pyrrolic unit to form five-, six-, seven-, and eight-membered fluorinated fused porphyrins.

Results and Discussion

Our previous work[7] showed that heating (30−40 °C) tetraarylporphyrins (TAP) with perfluoroalkyl iodides

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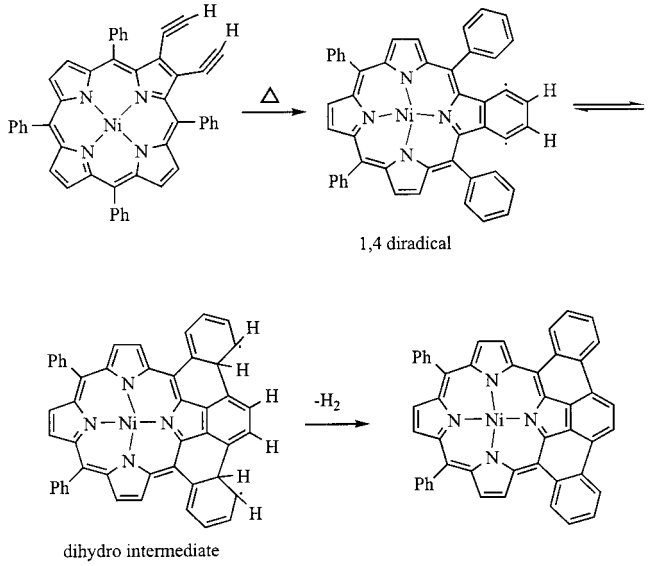
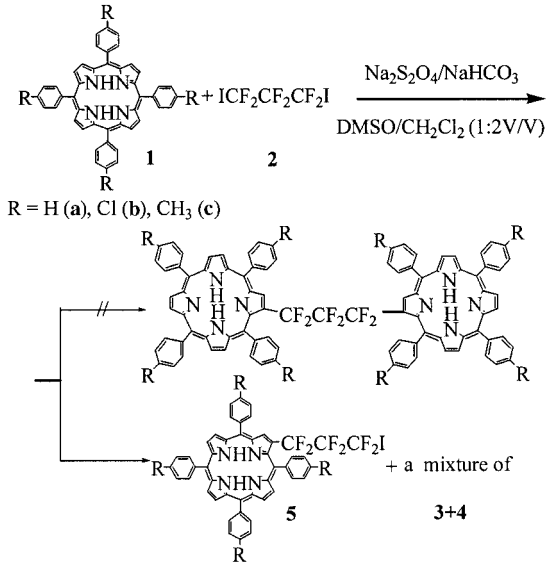


Scheme 2



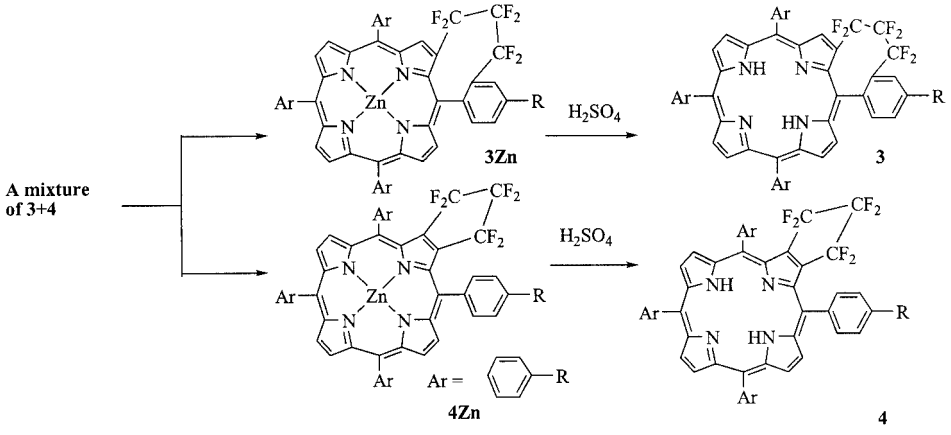
Scheme 3. The reaction of tetraarylporphyrins with 1,3-diiodohexafluoropropane

(R_FI) in $DMSO/CH_2Cl_2$ in the presence of $Na_2S_2O_4$/$NaHCO_3$ (the so-called sulfinatodehalogenation method)[8] for 14 h gives β-(perfluoroalkyl)tetraarylporphyrins. When a mixture of porphyrin (**1**) and 1,3-diiodohexafluoropropane (**2**) was heated at 55 °C for 22 h under the same conditions in the hope of preparing β,β-(hexafluoropropanediyl)-linked diporphyrins, we quite unexpectedly found that a mixture of 5,10,15-triaryl[2-benzohexafluoro(2^1,2^2,2^3)]-cyclooctanoporphyrins (**3**) and 5,10,15,20-tetraaryl-2-hexafluorocyclopentenylporphyrins (**4**) was obtained in 30% yield along with a trace of the normal adduct 5,10,15,20-tetraaryl-2-(iodohexafluoropropyl)porphyrins (**5**, 2%; Scheme 3).

A longer reaction time (22 h) is necessary for the formation of **3** and **4**, otherwise **5** is the major product (35%, 8 h). The mixture of **3** and **4** could not completely separated by normal column chromatography because of their very similar polarities. Fortunately, their zinc complexes were easily prepared and separated by flash column chromatography (**3Zn**, 43%; **4Zn**, 35%). Demetalation of **3Zn** and **4Zn** with concentrated H_2SO_4 resulted in the isolation of pure **3** and **4** in 90% yield each (Scheme 4).

The structures of **3**−**5** were unambiguously assigned by ^1H (^1H-^1H NOESY, DQCOSY, TOCOSY) and ^{19}F NMR spectroscopy, mass spectrometry, and elementary analysis. Single crystals of 5,10,15-triphenyl[2-benzohexafluoro-(2^2,2^3,2^4)]cyclooctanoporphyrin (**3a**) suitable for X-ray crystallography were obtained as rectangular purple plates from dichloromethane solutions into which petroleum ether was allowed to slowly diffuse. The aerial and edge views of **3a** are presented in Figure 1.

Figure 1 shows that the *meso*-phenyl groups are twisted due to the formation of an eight-membered ring. The torsion angle made by the *meso*-phenyl ring C39−C44 is 78.8°, whereas the *meso*-phenyl ring C33−C38 is almost orthogonal to the plane of the porphyrin macrocycle (the corresponding torsion angle is 86.9°); the other two *meso*-phenyl ring (C21−C26 and C27−C32) torsion angles are 54.62° and 53.52°, respectively. This shows that the *meso*-phenyl



Scheme 4. Metalation and demetalation reactions of **3** and **4**

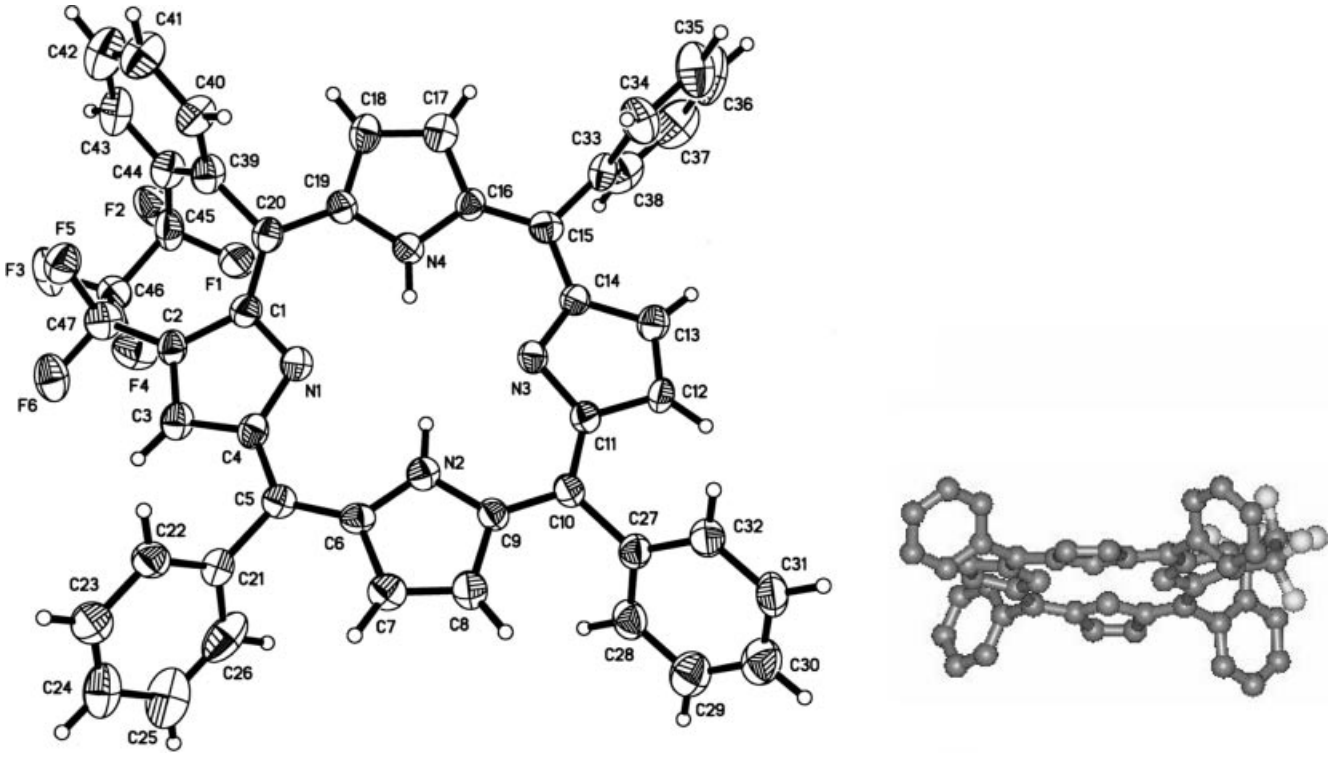


Figure 1. Aerial and side views of the X-ray crystal structure of **3a**

group C39−C44 rotates by about 25° during the course of the cyclization to form the eight-membered ring. The porphyrin macrocycles of **3a** show severe distortion due to the eight-membered ring strain. Analysis of the relative positions of the β-carbon atoms relative to the standard least-squares plane (C5−C10−C15−C20): the β-carbon atoms C7, C8, C17, and C18 lie below the plane, while C2, C3, C12, and C13 lie above the plane. Porphyrin **3a** therefore exists in a very nonplanar saddle conformation.

Single crystals of [2-(hexafluorocyclopentenyl)-5,10,15,20-tetraphenylporphinato]zinc(II) (**4aZn**) were obtained by slow concentration of a solution in hexane/dichloromethane to yield rectangular purple plates. The aerial and edge views of **4aZn** are presented in Figure 2.

The edge-on view of the macrocycle shows that the pyrrole rings of **4aZn** are alternately tilted up and down with respect to the least-squares plane of the 24 atoms of the porphyrin core; the macrocycle is distorted into a very nonplanar saddle conformation. The structure shows that the Zn−N4 distance is longer than the other three Zn−N bonds (i.e. Zn−N1, Zn−N2, Zn−N3); the difference in the Zn−N distances, Δ(Zn−N), is 0.03−0.04 Å. As reported previously,[10] the electronic effect of the β-substituents may also contribute to the different Zn−N distances — the strongly electron-withdrawing perfluoropropane group on the pyrrolic β-positions forms a five-membered ring and therefore decreases the electron density on N4; the weakened Zn−N4 bond is longer than the other Zn−N bonds. Figure 2 also shows the distortion between the perfluoropropane-containing five-membered ring (perfluoroalkyl part C21−C19) and the linked pyrrolic N4 ring: the dihedral angle between the two rings is about 14°.

To understand the reaction mechanism, some inhibition experiments were carried out. Addition of an electron-transfer scavenger — *p*-dinitrobenzene (20mol %) — or a free-radical inhibitor — hydroquinone (20mol %) — to the reaction mixture of **1a** and **2** decreased the yield of the mixture of **3a** and **4a** from 30% each to 15% and 10%, respectively, at the same reaction temperature and time (55 °C, 22 h).

On the basis of these experiments it appears that, as with R_FI,[7] $ICF_2CF_2CF_2$· may also be involved: **2** accepts one electron from the radical anion of sulfur dioxide, which is produced by decomposition of $Na_2S_2O_4$, and then dissociates to give iodide and $ICF_2CF_2CF_2^{\cdot}$, which then adds to the β,β-double bond of porphyrins to form the normal product **5**. The formation of **5** rather than 2,3-dihydroporphyrin (chlorin) may be ascribed to the solvent effect of DMSO[11] rather than to the rapid oxidation of unstable chlorin by the weak oxidants **2** and DMSO, as previously suggested in the case of R_FI.[7] Thus, both **3** and **4** maintain the original porphyrin conformations rather than the chlorin structures.

It also seemed possible that **5** might be an intermediate in the formation of **3** and **4**. This is indeed the case. Thus, heating **5** and $Na_2S_2O_4/NaHCO_3$ in $DMSO/CH_2Cl_2$ (1:2, v/v) at 55 °C for 6 h gave **3** and **4** in 50% yield with complete conversion of **5**. Thus, radical **A** derived from **5** is apparently the key species for constructing five- and eight-membered fused porphyrins (Scheme 5).

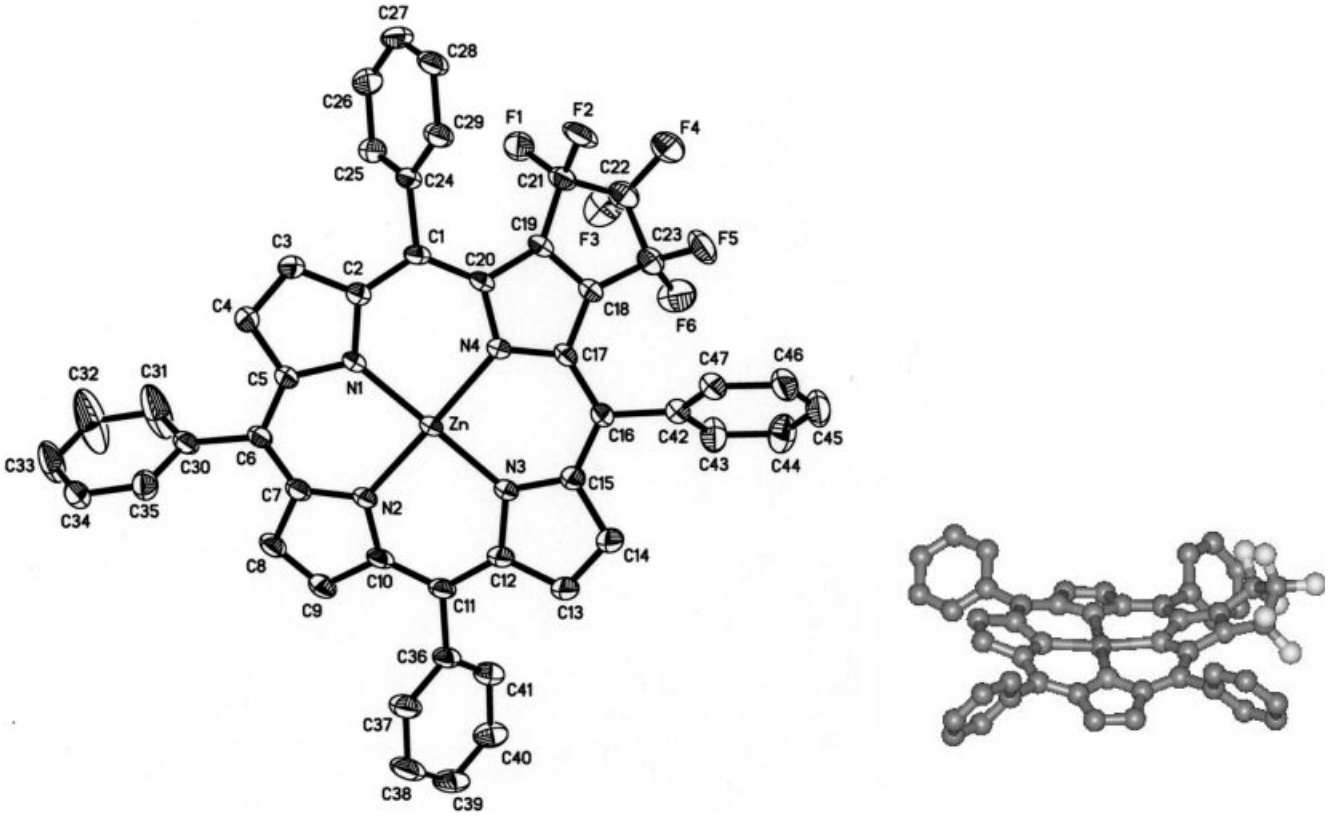
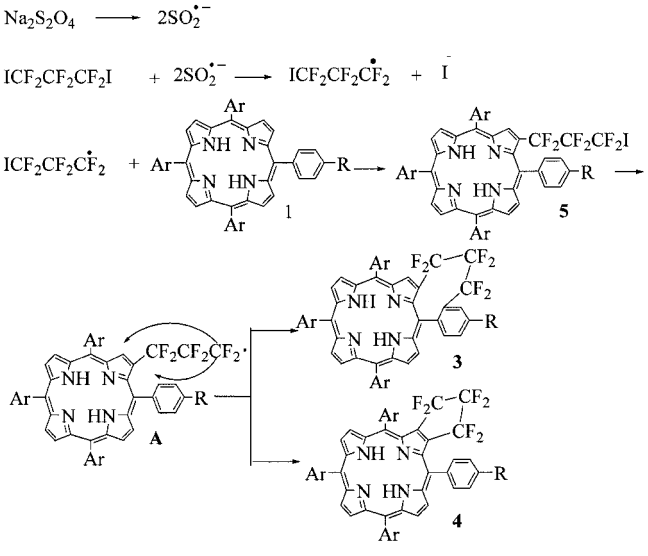


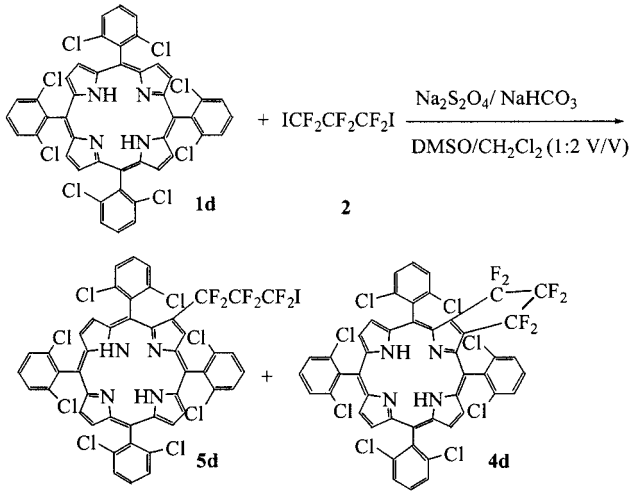
Figure 2. Aerial and side views of the X-ray crystal structure of **4aZn**



Scheme 5. A possible reaction mechanism for the formation of **3** and **4**

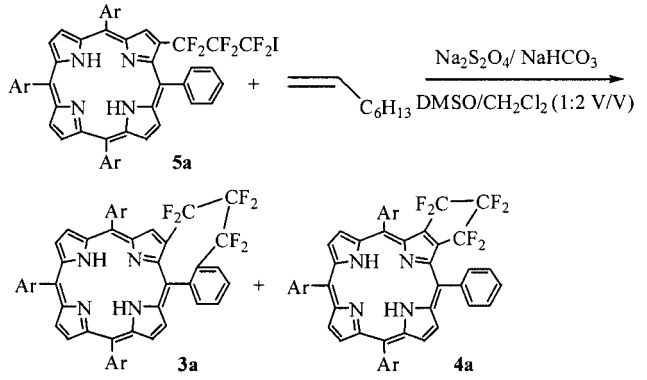
While the intramolecular attack of radical **A** at the β,β-double pyrrolic ring of porphyrin gives 5-*endo*,*trig* five-membered porphyrins rather than the 4-*exo*,*trig* four-membered ones predicted by Baldwin's rule,[12] a different intramolecular attack of radical **A** at the *ortho* position of the neighbouring *meso*-phenyl group forms the corresponding 8-*endo*,*trig* eight-membered compound.

Evidence that the *ortho* position of the *meso*-phenyl ring is attacked by radical **A** comes not only from the X-ray crystallographic data of **3a** and its NMR spectra but also from the fact that only **4** (10%) is produced if **2** is allowed to react with tetrakis(2,6-dichlorophenyl)porphyrin (**1d**), where all the *ortho* positions are occupied by chlorine atoms, under similar conditions (Scheme 6).



Scheme 6. The reaction of **1d** with 1,3-diiodohexafluoropropane

An attempt to trap the radical **A** with normal olefins (i.e. 1-octene) under similar sulfinatodehalogenation conditions met only with failure, **3** and **4** still being the sole products (Scheme 7).



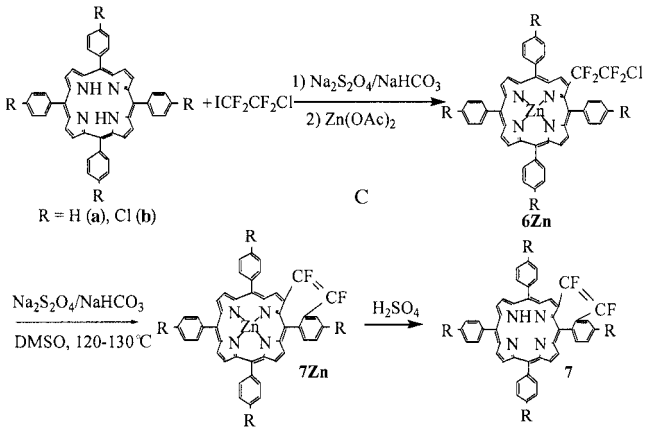
Scheme 7. The reaction of **5a** with 1-octene

The driving force for the cyclization of radical **A**, like the fluorinated terminal vinyl radicals [CH_2=$CH(CH_2)_m(CF_2)_n$ (m + n = 4, 5, 6)] that have been intensively investigated by Dolbier and co-workers,[13] comes most likely from the combination of an electrophilic perfluorinated radical with a nucleophilic porphyrinic alkene segment.[13b] Thus, the intramolecular cyclization of radical **A** occurs so fast that either dimerization of **A** or intermolecular addition of **A** to alkenes cannot compete.

The above results obtained with 1,3-diiodohexafluoropropane encouraged us to extend this approach to other α,ω-chloroiodo- or -diiodoperfluoroalkanes. We found that 1,2-diiodotetrafluoroethane does not react with tetraarylporphyrins under similar conditions, even at higher temperature (100 °C). This is probably due to the instability of $ICF_2CF_2^{\cdot}$, which easily decomposes to CF_2=CF_2.

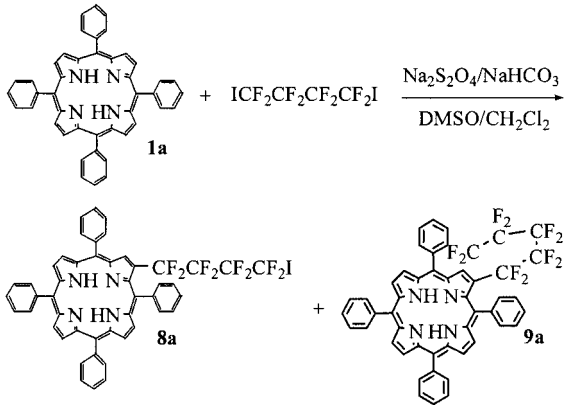
Like intermediate **5**, 5,10,15,20-tetraaryl-2-(chlorotetrafluoroethyl)porphyrins were synthesized in 38% yield by the reaction of $ClCF_2CF_2I$ with porphyrins in DMSO/CH_2Cl_2 (1:2, v/v) in the presence of $Na_2S_2O_4$/$NaHCO_3$ ($ClCF_2CF_2I$/TPP/$Na_2S_2O_4$/$NaHCO_3$ = 5:1:7.5:7.5) at 55 °C for 6 h. Then, making use of the activation of the carbon−chlorine bond of perfluoroalkyl chlorides in the sulfinatodehalogenation system at higher temperature,[8e] the intramolecular cyclization could be performed either with the free base $H_2TPPCF_2CF_2Cl$ (**6**) or, much better, with its zinc complexes (**6Zn**), in DMSO at 125 °C in the presence of a large excess of $Na_2S_2O_4$/$NaHCO_3$ (reactant ratio = 1:10:10) for 12 or 5 h, respectively (Scheme 8).

To our surprise only 5,10,15-triaryl[2-benzodifluoro (2^1,2^2)]cycloheptenoporphyrins were obtained, which means that the free radicals generated attack only at the *ortho* position of an adjacent phenyl group, with elimination of two fluorine atoms, to form a new conjugated π-system. The large red-shift of the Soret band (437 nm) and the Q bands (540, 613, 672 nm) of **7a** support this conclusion.



Scheme 8. The reaction of tetraarylporphyrins with $I(CF_2)_2Cl$

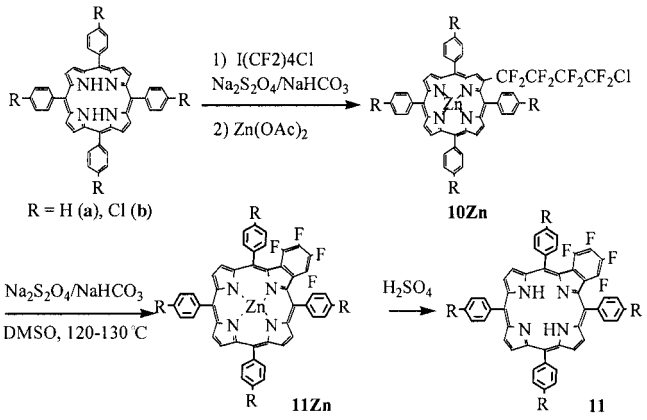
Treatment of $I(CF_2)_4I$ with tetraphenylporphyrin in DMSO/CH_2Cl_2 in the presence of $Na_2S_2O_4$/$NaHCO_3$ (reactant ratio = 1:1:3:3) at 55 °C for 22 h gave 5,10,15,20-tetraphenyloctafluorobenzoporphyrin in 30% yield in addition to a trace of the normal product iodooctafluorobutylporphyrin (**8a**, 2%; Scheme 9).



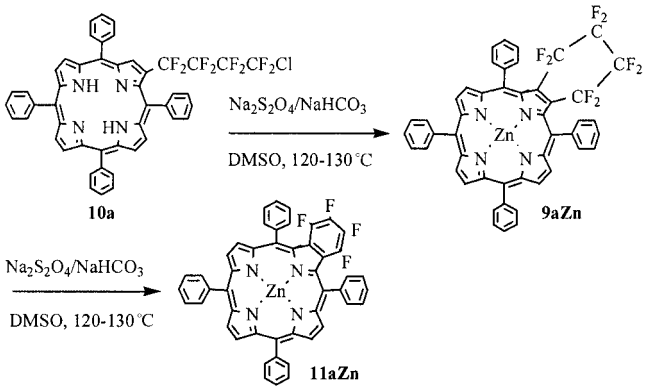
Scheme 9. The reaction of tetraarylporphyrins with 1,4-diiodooctafluorobutane

Interestingly, when $I(CF_2)_4Cl$ was used instead of $I(CF_2)_4I$, the initally formed $H_2TPP(CF_2)_4Cl$ (**10**) reacted under mild conditions with zinc, and could then be sulfinatodehalogenated with $Na_2S_2O_4$/$NaHCO_3$ (reactant ratio = 1:10:10) in DMSO at 120−130 °C for 5 h and finally treated with H_2SO_4 to afford β,β-(tetrafluorobenzo)porphyrins **11** (85%; Scheme 10).

In this reaction a small amount of [β-(octafluorocyclohexenyl)porphinato]zinc (**9aZn**) was also isolated and converted into **11aZn** after further treatment with $Na_2S_2O_4$/$NaHCO_3$, which suggests that the sulfur dioxide radical anion plays an important role in the fluorine elimination step at higher temperature (Scheme 11).



Scheme 10. The reaction of tetraarylporphyrins with $I(CF_2)_4Cl$



Scheme 11. The formation of β,β-(tetrafluorobenzo)porphyrins

The structure of **11aZn** was confirmed by an X-ray crystal-structure analysis. Crystallization of [tetraphenyl-β,β-(tetrafluorobenzo)porphinato]zinc (**11aZn**) was induced by slow concentration of a solution in petroleum ether/dichloromethane to yield rectangular purple plates. The aerial and edge views of **11aZn** are presented in Figure 3.

The edge-on view of the macrocycle shows that the pyrrole rings of **11aZn** are alternately tilted up and down with respect to the least-squares plane of the 24 atoms of the porphyrin core; the macrocycle is distorted into a very nonplanar saddle conformation. The angle between the least-squares plane of the macrocycle and the tetrafluorobenzene ring (C18−C24) is 18.88°, and that between the tetrafluorobenzene ring (C18−C24) and the pyrrolic N1 ring (N1−C17−C18−C19−C20) is 4.59°. These values indicate that the tetrafluorobenzene ring participates the macrocycle π-conjugation. In addition, the UV/Vis absorption spectrum of **11aZn** has a largely red-shifted Soret band (439 nm) and Q-band (570 nm), thus confirming the increase of π-conjugation in **11aZn**. The structure shows that Zn−N1 distance is longer than the other three Zn−N bond

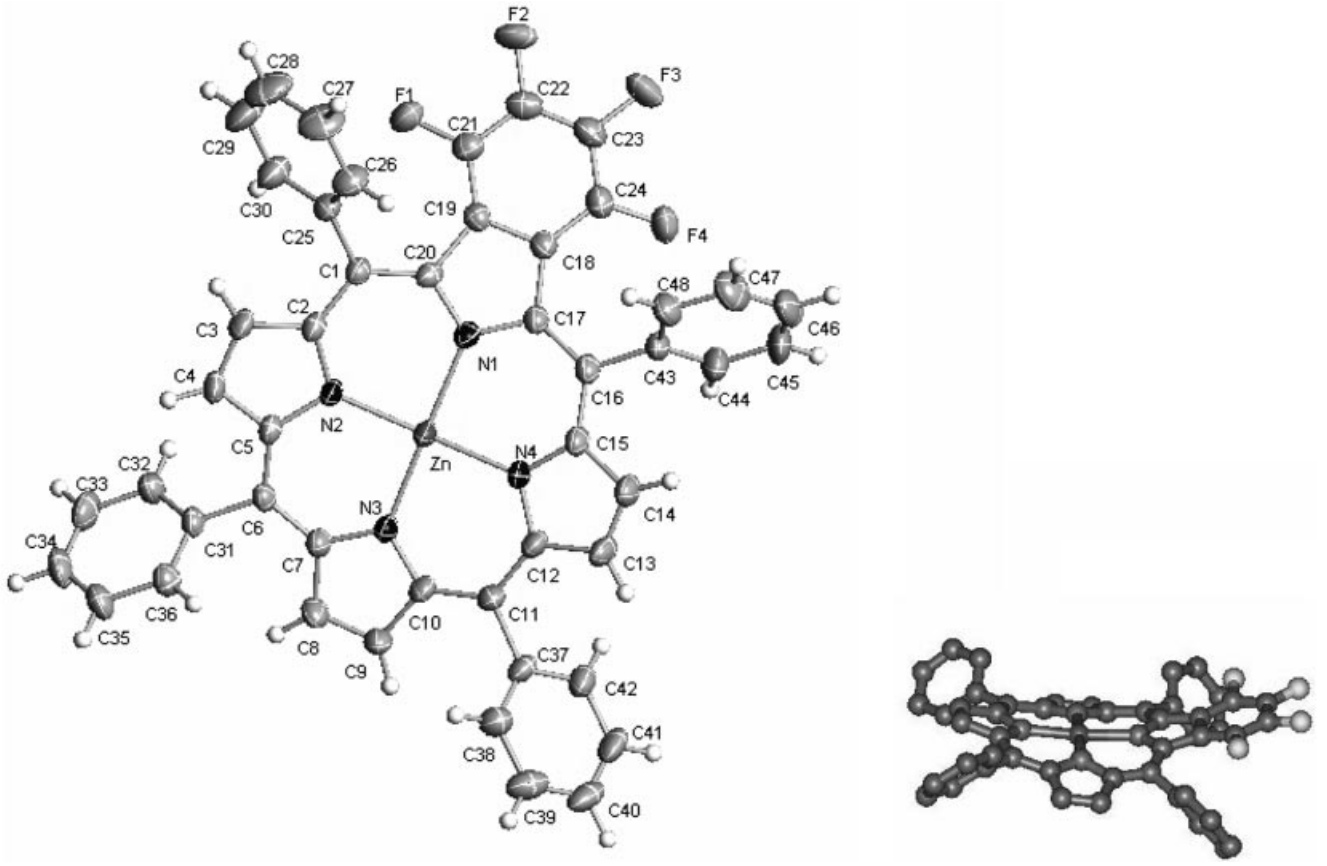
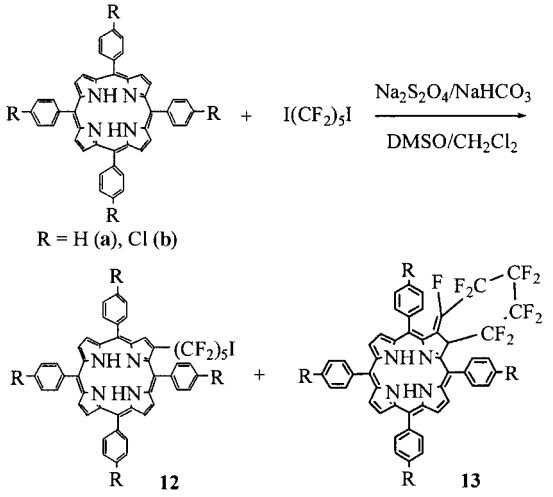


Figure 3. Aerial and side views of the X-ray crystal structure of **11aZn**

lengths as the tetrafluorobenzene ring on the pyrrolic N1 ring β-positions participates in the macrocycle π-conjugation, which results in a decrease of the electron density on N1 and thus a weakening of the Zn−N1 bond. The C18−C19−C21, C19−C21−C22, and C21−C22−C23 bond angles of the tetrafluorobenzene ring are approximately 119−120°, and therefore correspond to the bond angles expected for standard bezene-ring sp^2 carbon atoms.

Similar to 1,4-diiodooctafluorobutane, 1,5-diiodoperfluoropentane reacts with tetraarylporphyrins in DMSO/CH_2Cl_2 in the presence of $Na_2S_2O_4$/$NaHCO_3$ (reactant ratio = 1:1:3:3) at lower temperature (55 °C) to afford the unexpected fluorinated chlorin **13** (15%), in addition to a small amount of the normal, noncyclized product **12** (2%; Scheme 12).



Scheme 12. The reaction of tetraarylporphyrins with 1,5-diiododecafluoropentane

The structure of fluorinated chlorin **13** was established by ^{1}H NMR and UV/Vis spectroscopy (intense absorption of the Q band at 665 nm), mass spectrometry, and high-resolution mass spectrometry, although its ^{19}F NMR spectrum is too complicated to be completely assigned.

All the above reactions of porphyrins with ω-chloro(or -iodo)perfluoroalkyl iodides [$X(CF_2)_nI$; n = 2−5; X = Cl, I] under sulfinatodehalogenation conditions give different fluorinated fused porphyrins through a similar β-(perfluoroalkyl)porphyrin radical **A**, followed by its attack either at the *ortho* position of the neighbouring phenyl ring and/or adjacent pyrrolic unit, as suggested previously. The formation of a five-, six-, seven-, or eight-membered fused fluorinated porphyrin depends, apparently, on the chain length of the β-(perfluoroalkyl)porphyrin radical **A**, i.e., the chain length of $X(CF_2)_nI$, and consequently on the strain of the ring formed. The products formed under normal sulfinatodehalogenation conditions from the reactions with fluorinated diiodides [$I(CF_2)_nI$; n = 3−5] are simple five-, six-, or eight-membered fluorinated fused porphyrins, except for chlorin **13**, which is probably generated from (decafluoropentyl)porphyrin after defluorination by sulfur dioxide radical anion. When ω-chloroperfluoroalkyl iodides [$X(CF_2)_nI$; n = 2, 4; X = Cl] were used, two extensive six- and seven-membered π-conjugated fused prophyrins were obtained from tetraarylperfluorocycloalkenyl porphyrins after defluorination-aromatization under high-temperature sulfinatodehalogenation conditions.

Conclusion

In conclusion, we have presented a new intramolecular cyclization of β-(perfluoroalkyl)porphyrin radicals at the *ortho* position of a neighbouring phenyl ring as well as an adjacent pyrrolic unit to form five-, six-, seven-, or eight-membered fluorinated porphyrins depending on the chain length of $X(CF_2)_nI$ (n = 2−5; X = Cl, I) and, therefore, the strain strength of the rings formed by the sulfinatodehalogenation reaction of perfluoroalkyl iodides with porphyrins.

Experiment Section

General: ^{1}H NMR: ^{1}H-^{1}H NOESY, DQCOSY, TOCOSY) spectra were recorded with a Bruker AM-300 (300 MHz) and INOVA 600 (600 MHz) NMR spectrometer. ^{19}F NMR spectra were recorded with a Bruker AM-300 (282 MHz) spectrometer. Chemical shifts are reported in ppm relative to TMS as an internal standard (δ = 0 ppm) for ^{1}H NMR spectra and $CFCl_3$ as an external standard (negative for upfield) for ^{19}F NMR spectra. The solvent for NMR measurements was $CDCl_3$ (Aldrich). Mass and high-resolution mass spectra were recorded with a Hewlett−Packard HP-5989A spectrometer and a Finnigan MAT-8483 mass spectrometer. UV/Vis spectra were measured with a Varian Cary 100 spectrophotometer. All solvents and chemicals were reagent grade, purchased commericially, and used without further purification. Flash chromatography was performed using 300−400 mesh silica gel. Porphyrins H_2TPP (**1a**), H_2T(*p*-Cl)PP (**1b**), H_2T(*p*-CH_3)PP (**1c**), and H_2T(*o*,*o*-Cl_2)PP (**1d**) were prepared by literature methods.[14,15] Porphyrins **10a**, **10b**, and **10aZn** were prepared by a different literature method.[7]

General Procedure for the Preparation of Porphyrins 3 and 4: The porphyrin (0.4 mmol) was dissolved in a mixture of DMSO/CH_2Cl_2 (1:2, v/v; 30 mL) and then $ICF_2CF_2CF_2I$ (0.4 mmol), $Na_2S_2O_4$ (1.2 mmol), and $NaHCO_3$ (1.2 mmol) were added in this order. The mixture was stirred at 55 °C under argon for 22 h and the course of the reaction was monitored by TLC. After addition of 60 mL of CH_2Cl_2, the mixture was washed with water three times. The organic layer was dried with anhydrous Na_2SO_4 and then concentrated to dryness. The crude products were purified by column chromatography, using petroleum ether/dichloromethane (5:2 v/v) as eluent. The first dark-purple band was isolated and washed with CH_2Cl_2 to give a mixture of **3** and **4** (isolated yields: **3a** + **4a**: 30%; **3b** + **4b**: 26%; **3c** + **4c**: 15%). The second weak dark-purple band was also isolated and washed with CH_2Cl_2 to give 5,10,15,20-tetraaryl-β-(iodohexafluoropropyl)porphyrin (**5**) in 2% isolated yield. The third red-purple band was the unconsumed starting material **1**.

β-(Iodohexafluoropropyl)-5,10,15,20-Tetraphenylporphyrin (5a): ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.58 (s, 2 H, N−H), 7.65−7.82 (m, 12 H, Ph-H), 8.11−8.26 (m, 8 H, Ph-H), 8.69−8.91 (m, 6 H, β-H), 9.05 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −56.04 (s, 2 F, CF_2I), −96.56 (s, 2 F, $-CF_2CF_2CF_2I$), −109.27 (s,

2 F, $-CF_2CF_2I$) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 654 (1), 598 (0.55), 557 (0.70), 521 (1.98), 422 (42.80) nm. MS (EI): m/z = 891 [M^+ + 1]. HRMS (FT-MS) calcd. for $C_{47}H_{29}F_6IN_4{\cdot}H^+$: 891.1439; found 891.1414.

Metal Insertion into 3 and 4: The mixture of **3** amd **4** (30 mg) was dissolved in 30 mL of CH_2Cl_2 and treated with methanolic $Zn(OAc)_2{\cdot}2H_2O$ (50 mg in 30 mL methanol). The mixture was heated at reflux for 1 h. Silica gel (0.5 g) was added to the reaction mixture. The solvent was evaporated and the residue subjected to flash chromatography [silica gel, petroleum ether/dichloromethane (2:1)] to yield two fractions. The first, red-blue band afforded {5,10,15-triaryl[2-benzohexafluoro(2^2,2^3,2^4)]cyclooctanoporphinato}zinc(II) (**3Zn**; isolated yield: 40−50%) and the second, blue band yielded [5,10,15,20-tetraaryl-2-(hexafluorocyclopentenyl)-porphinato]zinc(II) (**4Zn**; isolated yield: 40−50%).

3aZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27−7.82 (m, 12 H, Ph-H), 7.92−8.37 (m, 7 H, Ph-H), 8.51 (d, J = 5.1 Hz, 1 H, β-H), 8.83−8.93 (m, 4 H, β-H), 9.43 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −92.67 (d, J = 270.7 Hz, 1 F, β-CF_2), −100.99 (d, J = 256.6 Hz, 1 F, β-CF_2), −112.85 (d, J = 265.1 Hz, 1 F, Ph−CF_2), −118.84 (d, J = 256.6 Hz, 1 F, Ph−CF_2), −130.30 (s, 2 F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 594 (1.0), 555 (2.19), 425 (56.31) nm. MS (EI): m/z = 825 [M^+ + 1]. $C_{47}H_{26}F_6N_4Zn{\cdot}1.5H_2O$ (851.15): calcd. C 66.27, H 3.40, N 6.58; found C 66.19, H 3.70, N 6.26.

3bZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56−7.82 (m, 8 H, Ph-H), 7.94−8.30 (m, 7 H, Ph-H), 8.55 (d, J = 4.8 Hz, 1 H, β-H), 8.83−8.99 (m, 5 H, β-H), 9.42 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −92.40 (d, J = 267.9 Hz, 1 F, β-CF_2), −101.80 (d, J = 256.6 Hz, 1 F, β-CF_2), −112.80 (d, J = 265.1 Hz, 1 F, Ph−CF_2), −118.68 (d, J = 256.6 Hz, 1 F, Ph−CF_2), −130.16 (s, 2 F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 596 (1.0), 556 (2.08), 426 (51.94) nm. MS (EI): m/z = 960 [M^+ + 1]. HRMS (FT-MS) calcd. for $C_{47}H_{22}Cl_4F_6N_4Zn{\cdot}H^+$: 960.9848; found 960.9867.

3cZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.72 (m, 12 H, CH_3), 7.53−7.61 (m, 8 H, Ph-H), 7.90−8.24 (m, 7 H, Ph-H), 8.52−8.95 (m, 6 H, β-H), 9.45 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −92.73 (d, J = 267.9 Hz, 1 F, β-CF_2), −100.81 (d, J = 253.8 Hz, 1 F, β-CF_2), −112.65 (d, J = 259.4 Hz, 1 F, Ph−CF_2), −118.83 (d, J = 251.0 Hz, 1 F, Ph−CF_2), −130.17 (s, 2 F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 598 (1.0), 557 (1.71), 427 (45.93) nm. MS (ESI): m/z = 881.2 [M^+ + 1]. HRMS (ESI) calcd. for $C_{51}H_{34}F_6N_4Zn{\cdot}H^+$: 881.2058; found 881.2052.

4aZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70−7.85 (m, 12 H, Ph-H), 8.17−8.21 (m, 8 H, Ph-H), 8.82 (AB, J = 5.1 Hz, 4 H, β-H), 8.904 (s, 2 H, β-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.89, 122.36, 126.08, 126.78, 127.85, 128.50, 132.49, 133.34, 134.35, 134.45, 134.69, 141.05, 141.88, 150.96, 152.22, 152.51 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −100.60 (s, 4 F, =CCF_2), −123.85 (s, 2 F, −CF_2CF_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 600 (1.0), 557 (1.25), 427 (35.39) nm. MS (EI): m/z = 825 [M^+ + 1]. $C_{47}H_{26}F_6N_4Zn{\cdot}1.5H_2O$ (851.15): calcd. C 66.27, H 3.40, N 6.58; found C 66.19, H 3.78, N, 6.26.

4bZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70−7.78 (m, 8 H, Ph-H), 8.09−8.11 (m, 8 H, Ph-H), 8.82 (AB, J = 4.9, 4 H, β-H), 8.90 (s, 2 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −100.04 (s, 4 F, =CCF_2), −123.60 (s, 2 F, −CF_2CF_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 598 (1.0), 558 (1.29), 427 (34.53) nm. MS (EI): m/z = 960 [M^+ + 1]. $C_{47}H_{22}Cl_4F_6N_4Zn{\cdot}H_2O$ (977.99): calcd. C 57.67, H 2.45, N 5.73; found C 57.65, H 2.62, N 5.48.

4cZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.72 (s, 12 H, CH_3), 7.50−7.58 (m, 8 H, Ph-H), 8.04~8.08 (m, 8 H, Ph-H), 8.78−8.89 (m, 6 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −100.45 (s, 4 F, =CCF_2), −123.15 (s, 2 F, −CF_2CF_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 601 (1.0), 558 (1.20), 428 (26.25) nm. MS (ESI): m/z = 881.2 [M^+ + 1]. HRMS (ESI) calcd. for $C_{51}H_{34}F_6N_4Zn{\cdot}H^+$: 881.2071; found 881.2052.

Demetalation of 3Zn and 4Zn: A sample of **3Zn** or **4Zn** (30 mg) was dissolved in 50 mL of CH_2Cl_2 and treated with concentrated sulfuric acid (0.5 mL) over 3 min. The organic layer was washed with water (3 × 50 mL) and then dried with anhydrous sodium sulfate. The solvent was evaporated and the residue subjected to flash chromatography [silica gel, petroleum ether/dichloromethane (1:1)] to give **3** or **4** (isolated yield: 90% in each case).

3a: ^{1}H NMR (600 MHz, $CDCl_3$): δ = −2.49 (s, 2 H, N−H), 7.62 (d, J = 7.8 Hz, 1 H, Ph-H),[16] 7.68−7.83 (m, 10 H, Ph-H), 7.89 (t, J = 7.8 Hz, 1 H, Ph-H), 7.97 (d, J = 5.4 Hz, 1 H, Ph-H), 8.04−8.11 (m, 3 H, Ph-H), 8.30−8.36 (m, 3 H, Ph-H), 8.49 (AB, J = 2.4 Hz, 1 H, β-H),[16] 8.72 (AB, J = 2.1 Hz, 1 H, β-H), 8.76 (AB, J = 2.4 Hz, 1 H, β-H), 8.78 (AB, J = 2.1 Hz, 1 H, β-H), 8.84 (AB, J = 4.8 Hz, 1 H, β-H), 8.86 (AB, J = 5.4 Hz, 1 H, β-H), 9.25 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −93.07 (d, J = 267.9 Hz, 1 F, β-CF_2), −100.49 (d, J = 256.6 Hz, 1 F, β-CF_2), −113.05 (d, J = 256.6 Hz, 1 F, Ph−CF_2), −118.64 (d, J = 256.6 Hz, 1 F, Ph−CF_2), −130.61 (s, 2 F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 656 (1.0), 599 (0.66), 559 (0.95), 521 (2.11), 423 (48.55) nm. MS (EI): m/z = 763 [M^+ + 1]. HRMS (FT-MS) calcd. for $C_{47}H_{28}F_6N_4{\cdot}H^+$: 763.2278; found 763.2291.

3b: ^{1}H NMR (600 MHz, $CDCl_3$): δ = −2.59 (s, 2 H, N−H), 7.55 (d, J = 8.4 Hz, 1 H, Ph-H),[16] 7.69−7.79 (m, 7 H, Ph-H), 7.89 (d, J = 6 Hz, 1 H, Ph-H), 7.95−8.00 (m, 2 H, Ph-H), 8.09 (s, 1 H, Ph-H), 8.20−8.26 (m, 3 H, Ph-H), 8.52 (AB, J = 4.2 Hz, 1 H, β-H),[16] 8.71 (AB, J = 4.8 Hz, 1 H, β-H), 8.75 (AB, J = 4.8 Hz, 1 H, β-H), 8.78 (AB, J = 5.4 Hz, 1 H, β-H), 8.83 (AB, J = 4.8 Hz, 1 H, β-H), 8.86 (AB, J = 4.8 Hz, 1 H, β-H), 9.22 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −92.78 (d, J = 267.9 Hz, 1 F, β-CF_2), −101.34 (d, J = 259.4 Hz, 1 F, β-CF_2), −113.01 (d, J = 267.9 Hz, 1 F, Ph−CF_2), −118.5 (d, J = 267.9 Hz, 1 F, Ph−CF_2), −130.49 (s, 2 F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 655 (1.0), 600 (0.66), 558 (1.00), 523 (2.40), 424 (62.20) nm. MS (EI): m/z = 899 [M^+ + 1]. HRMS (MALDI) calcd. for $C_{47}H_{29}Cl_4F_6N_4{\cdot}H^+$: 899.0710; found 899.0732.

4a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.68 (s, 2 H, N−H), 7.73−7.87 (m, 12 H, Ph-H), 8.19−8.25 (m, 8 H, Ph-H), 8.73 (s, 2 H, β-H), 8.87 (AB, J = 4.8 Hz, 4 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −101.71 (s, 4 F, =CCF_2), −123.55 (s, 2 F, −CF_2CF_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 662 (1.0), 605 (0.35), 526 (1.24), 425 (29.06) nm. MS (ESI): m/z = 763 [M^+ + 1]. HRMS (FT-MS) calcd. for $C_{47}H_{28}F_6N_4{\cdot}H^+$: 763.2287; found 763.2291.

4b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.78 (s, 2 H, N−H), 7.73−7.79 (m, 8 H, Ph-H), 8.10−8.15 (m, 8 H, Ph-H), 8.72 (s, 2 H, β-H), 8.88 (AB, J = 5.1, 4 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −101.21 (s, 4 F, =CCF_2), −123.36 (s, 2 F, −CF_2CF_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 662 (1.0), 604 (0.28), 526 (1.21), 425 (30.32) nm. MS (EI): m/z = 899 [M^+ + 1]. HRMS (FT-MS) calcd. for $C_{47}H_{24}Cl_4F_6N_4{\cdot}H^+$: 899.0738; found 899.0732.

Synthesis of 4d: Porphyrin **1d** (0.4 mmol) was dissolved in a mixture of DMSO and CH_2Cl_2 (1:2, v/v; 30 mL), and then $ICF_2CF_2CF_2I$ (0.4 mmol), $Na_2S_2O_4$ (1.2 mmol), and $NaHCO_3$ (1.2 mmol) were added in this order. The mixture was stirred at 55 °C under argon for 22 h and the course of the reaction was monitored by TLC. After addition of 60 mL of CH_2Cl_2, the mixture was washed with water three times. The organic layer was dried with anhydrous Na_2SO_4 and concentrated to dryness. The crude products were purified by column chromatography, using petroleum ether/dichloromethane (3:1) as eluent. The first, dark-purple band was isolated and washed with CH_2Cl_2 to give **4d** (isolated yield: 10%). The second, weak, dark-purple band contained **5d**, and the third, red-purple band contained the unconsumed starting material **1d**. Porphyrins **5d** and **1d** could not be completely separated by column chromatography because of their very similar polarities. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.48 (s, 2 H, N-H), 7.70−7.84 (m, 12 H, Ph-H), 8.56 (s, 2 H, β-H), 8.71−8.75 (m, 4 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −103.28 (s, 4 F, =CCF$_2$), −121.19 (s, 2 F, −CF$_2$C*F*$_2$) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 656 (1.0), 599 (0.75), 523 (2.19), 424 (43.81) nm. MS (MALDI): *m*/*z* = 1035 [M$^+$ + 1]. $C_{47}H_{20}Cl_8F_6N_4{\cdot}H_2O$ (1051.92): calcd. C 53.66, H 2.16, N 5.32; found C 53.49, H 2.37, N 4.83.

General Procedure for the Preparation of Porphyrins 6 and Metalated Porphyrins 6Zn: The porphyrin (0.6 mmol) was dissolved in a mixture of DMSO and CH_2Cl_2 (1:2, v/v; 150 mL), and then $ClCF_2CF_2I$ (3.0 mmol), $Na_2S_2O_4$ (4.5 mmol), and $NaHCO_3$ (4.5 mmol) were added in that order. The mixture was stirred at 55 °C under argon for 6 h and the course of the reaction was monitored by TLC. After addition of 100 mL of CH_2Cl_2, the mixture was washed with water three times. The organic layer was dried with anhydrous Na_2SO_4 and concentrated to dryness. The crude products were purified by column chromatography, using petroleum ether/dichloromethane (3:1) as eluent. The red-purple band and the dark-purple band were isolated and washed with CH_2Cl_2. The red-purple band was unconsumed starting material. The dark-purple band was further purified by flash chromatography [300−400 mesh silica gel, petroleum ether/dichloromethane (5:1)] to yield **6** as a light-purple solid (yield: 35%). Metal insertion into the porphyrin was similar to that described above for the preparation of **3Zn** and **4Zn**.

Porphyrin 6a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.60 (s, 2 H, N−H), 7.69−7.79 (m, 12 H, Ph-H), 8.14−8.25 (m, 8 H, Ph-H), 8.68−8.91 (m, 6 H, β-H), 9.08 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −66.53 (s, 2 F, −C*F*$_2$Cl), −94.65 (s, 2 F, −C*F*$_2$CF$_2$Cl) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 655 (1.6), 598 (1.0), 521 (3.4), 422 (77.2) nm. MS (EI): *m*/*z* = 748 [M$^+$ + 1]. $C_{46}H_{29}F_4N_4{\cdot}0.5H_2O$ (722.24): calcd. C 72.87, H 3.96, N 7.39; found C 73.07, H 4.15, N 7.28.

Porphyrin 6b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.60 (s, 2 H, N−H), 7.66−7.81 (m, 12 H, Ph-H), 8.05−8.17 (m, 8 H, Ph-H), 8.68−8.91 (m, 6 H, β-H), 9.06 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −66.53 (s, 2 F, −C*F*$_2$Cl), −94.65 (s, 2 F, −C*F*$_2$CF$_2$Cl) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 655 (1.5), 598 (1.0), 521 (3.5), 422 (73.7) nm. MS (ESI): *m*/*z* = 886 [M$^+$ + 1]. HRMS (MALDI) calcd. for $C_{46}H_{25}Cl_5F_4N_4{\cdot}H^+$: 885.0547; found 885.0531.

6aZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60−7.91 (m, 12 H, Ph-H), 8.11−8.22 (m, 8 H, Ph-H), 8.64−8.92 (m, 6 H, β-H), 9.34 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −65.85 (s, 2 F, −C*F*$_2$Cl), −93.49 (s, 2 F, −C*F*$_2$CF$_2$Cl) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 593 (1.0), 553 (1.9), 423 (46.7) nm. MS (ESI): *m*/*z* = 811 [M$^+$ + 1]. HRMS (MALDI) calcd. for $C_{46}H_{27}ClF_4N_4Zn{\cdot}H^+$: 811.1208; found 811.1225.

General Procedure for the Preparation of 7Zn: The porphyrin **6Zn** (0.1 mmol) was dissolved in 20 mL of DMSO and then $Na_2S_2O_4$ (1.0 mmol) and $NaHCO_3$ (1.0 mmol) were added in that order. The mixture was stirred at 125 °C under argon for 5 h and the course of the reaction was monitored by TLC. After addition of 40 mL of CH_2Cl_2, the mixture was washed with water three times. The organic layer was dried with anhydrous Na_2SO_4 and the solvents were evaporated to dryness. The crude products were purified by flash chromatography [300−400 mesh silica gel, petroleum ether/dichloromethane (1:1)] to yield **7Zn** as a light-purple solid (yield: 86%).

7aZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44−8.02 (m, 16 H, Ph-H), 8.49 (t, *J* = 8.1 Hz, 2 H), 8.68 (d, *J* = 6.9 Hz, 1 H), 8.85−9.10 (m, 6 H), 9.29 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −130.18 (d, *J* = 16.6 Hz, 1 F, =CF), −141.09 (d, *J* = 16.9, 1 F, =CF) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 621 (1.0), 574 (1.4), 444 (21.7) nm. MS (MALDI): *m*/*z* = 736.1 [M$^+$]. HRMS (MALDI) calcd. for $C_{46}H_{26}F_2N_4Zn{\cdot}H^+$: 737.1038; found 737.1156.

7bZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63−7.92 (m, 12 H, Ph-H), 8.34−9.25 (m, 10 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −127.99 (d, *J* = 16.9 Hz, 1 F, =CF), −140.02 (d, *J* = 14.1 Hz, 1 F, =CF) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 621 (1.0), 576 (1.2), 446 (21) nm. MS (ESI): *m*/*z* = 873 [M$^+$ + 1]. HRMS (MALDI) calcd. for $C_{46}H_{22}Cl_4F_2N_4Zn{\cdot}H^+$: 872.9959, found 872.9931. $C_{46}H_{22}N_4F_2Cl_4Zn{\cdot}3H_2O$ (926.02): calcd. C 59.66, H 3.04, N 6.05; found C 60.13, H 2.62, N 5.69.

The procedure for the demetalation of **7Zn** to give **7** is the same as that for preparing **3** and **4**.

Porphyrin 7a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.25 (s, 2 H, N−H), 7.63−7.88 (m, 16 H, Ph-H), 8.57 (t, *J* = 8.4 Hz, 2 H), 8.75−9.20 (m, 9 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −130.31 (d, *J* = 17.5 Hz, 1 F, =CF), −140.56 (d, *J* = 19.5 Hz, 1 F, =CF) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 672 (1.9), 613 (1.0), 540 (3.3), 437 (77.2) nm. MS (ESI): *m*/*z* = 675 [M$^+$ + 1]. $C_{48}H_{24}Cl_4F_4N_4{\cdot}H_2O$ (890.08): calcd. C 64.71, H 2.92, N 6.29; found C 64.78, H 2.77, N 6.16.

Porphyrin 7b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.34 (s, 2 H, N−H), 7.53−7.93 (m, 12 H, Ph-H), 8.45−8.59 (m, 3 H), 8.77 (AB, *J* = 4.8 Hz, 2 H), 8.92−9.21 (m, 5 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −127.96 (d, *J* = 16.6 Hz, 1 F, =CF), −140.26 (d, *J* = 18.3 Hz, 1 F, =CF) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 672 (1.6), 614 (1.0), 582 (1.4), 541 (3.0), 441 (40.1) nm. MS (ESI): *m*/*z* = 811 [M$^+$ + 1]. HRMS (MALDI) calcd. for $C_{46}H_{25}Cl_4F_2N_4{\cdot}H^+$: 811.0820; found 811.0796.

The procedure for the preparation of **8a** and **9a** was similar to that for the preparation of **4d**.

8a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.59 (s, 2 H, N−H), 7.28−7.85 (m, 12 H, Ph-H), 8.12−8.27 (m, 8 H, Ph-H), 8.69−8.79 (m, 4 H, β-H), 8.87−8.93 (m, 2 H, β-H), 9.06 (s, 1 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −58.17 (s, 2 F, −C*F*$_2$I), −97.49 (s, 2 F, =CCF$_2$), −112.35 (s, 2 F, −C*F*$_2$CF$_2$I), −117.13 (s, 2 F, −CF$_2$CF$_2$) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 657 (1.9), 603 (1.0), 560 (1.1), 522 (3.2), 424 (77.1) nm. MS (ESI): *m*/*z* = 940 [M$^+$ + 1]. $C_{48}H_{29}F_8IN_4$ (940.13): calcd. C 61.29, H 3.11, N 5.96; found C 61.60, H 3.33, N 5.67.

9a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.12 (s, 2 H, N−H), 7.76−7.79 (m, 12 H, Ph-H), 8.19−8.26 (m, 8 H, Ph-H), 8.56 (s, 2 H, β-H), 8.75 (AB, J = 4.8 Hz, 4 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −95.58 (s, 4 F, =CCF_2), −133.76 (s, 4 F, −CF_2CF_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 695 (4.5), 642 (1.2), 581 (1.0), 538 (3.4), 439 (73.7) nm. MS (EI): m/z = 813 [M^+ + 1]. HRMS (FTMS) calcd. $C_{48}H_{29}F_8N_4{\cdot}H^+$: 813.2270; found 813.2259.

The general procedure for the preparation of **11Zn** was similar to that for the preparation of **7Zn**.

11aZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64−7.80 (m, 12 H, Ph-H), 8.11−8.24 (m, 8 H, Ph-H), 8.68−8.81 (m, 6 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −94.60 (s, 4 F, =CCF_2), −133.80 (s, 4 F, −CF_2CF_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 621 (1.5), 568 (1.0), 436 (29.3) nm. MS (ESI): m/z = 798 [M^+ + 1]. $C_{48}H_{26}F_4N_4Zn$ (798.14): calcd. C 72.05, H 3.28, N 7.00; found C 70.34, H 3.68, N 6.78.

11bZn: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75−7.80 (m, 8 H, Ph-H), 8.13−8.16 (m, 8 H, Ph-H), 8.79−8.85 (m, 6 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −128.79 (d, J = 17.2 Hz, 2 F, =CF), −155.44 (d, J = 18 Hz, 2 F, =CF) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 569 (1.0), 440 (23.1) nm. MS (ESI): m/z = 935 [M^+ + 1]. $C_{48}H_{22}Cl_4F_4N_4Zn{\cdot}3H_2O$ (988.01): calcd. C 58.30, H 2.83, N 5.66; found C 58.06, H 2.44, N 5.36.

9aZn: A small amout of **9aZn** (6%) was isolated from the same reaction mixture. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64−7.80 (m, 12 H, Ph-H), 8.11−8.24 (m, 8 H, Ph-H), 8.68−8.81 (m, 6 H, β-H) ppm.^{19}F NMR (282 MHz, $CDCl_3$): δ = −94.60 (s, 4 F, =CCF_2), −133.80 (s, 4 F, −CF_2CF_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 621 (1.5), 568 (1.0), 436 (29.3) nm. MS (ESI): m/z = 875 [M^+ + 1]. HRMS (MALDI) calcd. for $C_{48}H_{26}F_8N_4Zn{\cdot}H^+$: 875.1375; found 875.1394.

The demetalation of **11Zn** to give **11** was similar to that for the preparation of **7**.

Porphyrin 11a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.36 (s, 2 H), 7.81 (s, 12 H, Ph-H), 8.27 (m, 4 H, Ph-H), 8.35 (m, 4 H, Ph-H), 8.62 (s, 2 H, β-H), 8.75 (d, J = 5.1 Hz, 2 H), 8.91 (d, J = 5.1 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −131.38 (m, 2 F, =CF), −156.95 (m, 2 F, =CF) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 677 (1.0), 614 (1.4), 535 (4.4), 439 (84.9) nm. MS (EI): m/z = 736 [M^+ + 1]. $C_{48}H_{24}F_4N_4$ (732.19): calcd. C 78.25, H 3.83, N 7.60; found C 77.92, H 4.24, N 7.16.

Porphyrin 11b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.44 (s, 2 H), 7.81 (d, J = 6 Hz, 8 H, Ph-H), 8.17−8.28 (m, 8 H, Ph-H), 8.61 (s, 2 H), 8.74 (d, J = 4.8 Hz, 2 H, β-H), 8.86 (d, J = 5.1 Hz, 2 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −130.69 (d, J = 21.4 Hz, 2 F, =CF), −155.68 (d, J = 16.9 Hz, 2 F, =CF) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 681 (1.0), 614 (2.2), 536 (11.9), 441 (26.5) nm. MS (ESI): m/z = 873 [M^+ + 1]. $C_{48}H_{24}Cl_4F_4N_4{\cdot}H_2O$ (890.08): calcd. C 64.71, H 2.92, N 6.29; found C 64.78, H 2.77, N 6.16.

The procedure for the preparation of **12** and **13** was similar to that for preparing **4d**.

Porphyrin 12b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −2.66 (s, 2 H, N−H), 7.65−7.82 (m, 8 H, Ph-H), 8.03−8.19 (m, 8 H, Ph-H), 8.68−9.05 (m, 7 H, β-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −58.65 (s, 2 F), −97.08 (s, 2 F), −113.36 (s, 2 F), −118.16 (s, 2 F), −120.42 (s, 2 F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 654 (1.3), 597 (1.0), 550 (1.3), 519 (3.7), 420 (64.3) nm. MS (MALDI): m/z = 1126.7 [M^+ + 1]. HRMS (MALDI) calcd. for $C_{49}H_{25}N_4F_{10}Cl_4I{\cdot}H^+$: 1126.9816; found 1126.9791.

Porphyrin 13a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −1.92 (s, 2 H, N−H), 6.49 (d, J = 27 Hz, 1 H, CH), 7.57−7.81 (m, 12 H), 7.86−8.07 (m, 6 H), 8.26−8.38 (m, 4 H), 8.44−8.64 (m, 4 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 665 (2.8), 609 (1.0), 562 (1.6), 437 (20.3), 423 (28.6) nm. MS (EI): m/z = 845 [M^+ + 1]. HRMS (MALDI) calcd. for $C_{49}H_{29}N_4F_9{\cdot}H^+$: 845.2334; found 845.2321.

Porphyrin 13b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = −1.56 (s, 2 H, N−H), 6.44 (d, J = 26 Hz, 1 H, CH), 7.59−8.05 (m, 18 H), 8.22−8.49 (m, 6 H), 8.62−8.67 (m, 2 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (relative intensity) = 665 (2.6), 610 (1.0), 563 (1.6), 530 (1.9), 420 (27.7) nm. MS (EI): m/z = 982 [M^+ + 1]. HRMS (MALDI) calcd. for $C_{49}H_{25}N_4F_9Cl_4{\cdot}H^+$: 981.0762; found 981.0762.

X-ray Crystallographic Studies: Crystals for the X-ray analyses were obtained as described above. The crystals were mounted on glass fibers or sealed in thin-walled glass capillaries. The X-ray intensity data for **3a**, **4aZn**, and **11aZn** were collected with a SMART APEX diffractometer employing Mo-K_α radiation (λ = 0.71073 Å) and using the ω-2θ scan technique. The intensity data were corrected for Lorentz and polarization effects. Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Crystal data and data collection parameters are summarized in Table 1. CCDC-244097 (**3a**), -244098 (**4aZn**), and -244099 (**11aZn**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information (see also footnote on the first page of this article): ^{1}H and ^{19}F NMR, mass, and UV/Vis spectra of all new compounds and ^{1}H NMR (^{1}H-^{1}H NMR, DQCOSY, TOCOSY) spectra of **3a**.

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Table 1. Crystal data and structure refinement for porphyrins **3a**, **4aZn**, and **11aZn**

	3a	**4aZn**	**11aZn**
Empirical formula	$C_{47}H_{28}F_6N_4$	$C_{47}H_{26}F_6N_4Zn$	$C_{48}H_{26}F_4N_4Zn{\cdot}2CH_2Cl_2$
Formula mass	762.73	826.09	969.95
Dimensions [mm]	0.475 × 0.368 × 0.204	0.528 × 0.390 × 0.145	0.506 × 0.239 × 0.218
Crystal system	monoclinic	triclinic	triclinic
T [K]	293(2)	293(2)	293(2)
a [Å]	13.938(4)	11.7494(11)	11.035(4)
b [Å]	17.120(5)	12.0508(11)	13.363(5)
c [Å]	15.908(5)	14.5688(13)	15.372(6)
α [°]	90	67.6100(10)	96.927(7)
β [°]	107.972(6)	80.782(2)	99.307(7)
γ [°9	90	74.891(2)	104.919(7)
V [Å^3]	3610.6	1837.1	2130.1
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
μ(Mo-K_α) [mm^{-1}]	0.71073	0.71073	0.71073
R_1	0.0662	0.0545	0.0907
Reflections measured	3528	11042	133055
$2\theta_{max}$ [°]	56.44	56.44	56.64

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