Fluoroalkylation of Porphyrins: Synthesis of Porphyrins Bearing Double *meso*,β-Fused Fluoroalkyl Rings via Radical Cyclization

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Received 2 February 2007

Abstract: A series of fluorinated *meso*,β-fused 5,15-diphenylporphyrins have been synthesized by the reaction of 5,15-diphenylporphyrins with fluoroalkyl halides under modified sulfinatodehalogenation reaction conditions through radical cyclization.

Key words: fluoroalkylation, fused porphyrins, radical cyclization, fluoroalkyl iodides, sulfinatodehalogenation

Porphyrins, a class of tetrapyrrolic macrocycles, have found a wide applications ranging from catalysts,[1] materials, and devices[2] to photodynamic therapeutic agents (PDT).[3] However, most of their applications require modification of the porphyrin macrocycle to allow attachment of additional substituents with various other functionalities. Such modifications have led to the synthesis of contracted, expanded, or isomeric porphyrinic compounds.[4] Within this diversity of porphyrin chemistry, there has been much interest in the synthesis of porphyrins bearing fused rings, whether as extensions of the conjugated macrocycle or fused alicyclic ring systems. Porphyrins with fused exocyclic rings have proved to be valuable research tools and a fruitful area for the development of synthetic methodology.[5] Lash and co-workers made detailed investigations into the synthesis and properties of various porphyrins with exocyclic rings.[6] During our investigation on the fluoroalkylation of tetraarylporphyrins, a series of porphyrins fused with five-, six-, seven-, and eight-membered fluorinated rings have been synthesized through a fluorinated porphyrin intramolecular radical cyclization during the reaction of $I(CF_2)_nX$ (n = 2–5; X = Cl, I) with tetraarylporphyrins under modified sulfinatodehalogenation conditions.[7] For 5,10,15-triaryl-porphyrins, 5,10,15-triaryl-2,20-(hexafluoropropanediyl) porphyrins were obtained very recently in our laboratory from *meso*- or β-(3-idohexafluoropropyl)porphyrins under similar conditions.[8]

Meanwhile, Gouterman[9] showed that several fluorinated fused porphyrins were observed as the fragments in the electrospray ionization (ESI) mass-spectrometric analysis in positive and negative modes of *meso*-tetrakis(heptafluoropropyl)porphyrin. The formation of the fragments with direct covalent *meso*-alkyl-to-β-linkages on elimination of HF was proposed. It would be interesting to evaluate whether the same fragmentation pattern of fluorinated porphyrins is valid in the solution-phase reactions. In connection with this problem, we herein report our results.

Heating 5,15-diphenylporphyrin (**1**) with 1,3-diiodohexafluoropropane (**2**) in the presence of $Na_2S_2O_4/NaHCO_3$ (molar ratio = 1:1:1:1) in DMSO–CH_2Cl_2 (v/v = 1:1) at 65 °C for 4 hours yielded a mixture of a monofluoroalkylated porphyrins **3** (26%), **4** (20%), and unchanged starting material **1** (40%, Scheme 1). Compounds **3** and **4** were readily metalated in the presence of $Zn(OAc)_2$ to form **Zn·3** and **Zn·4**, respectively.

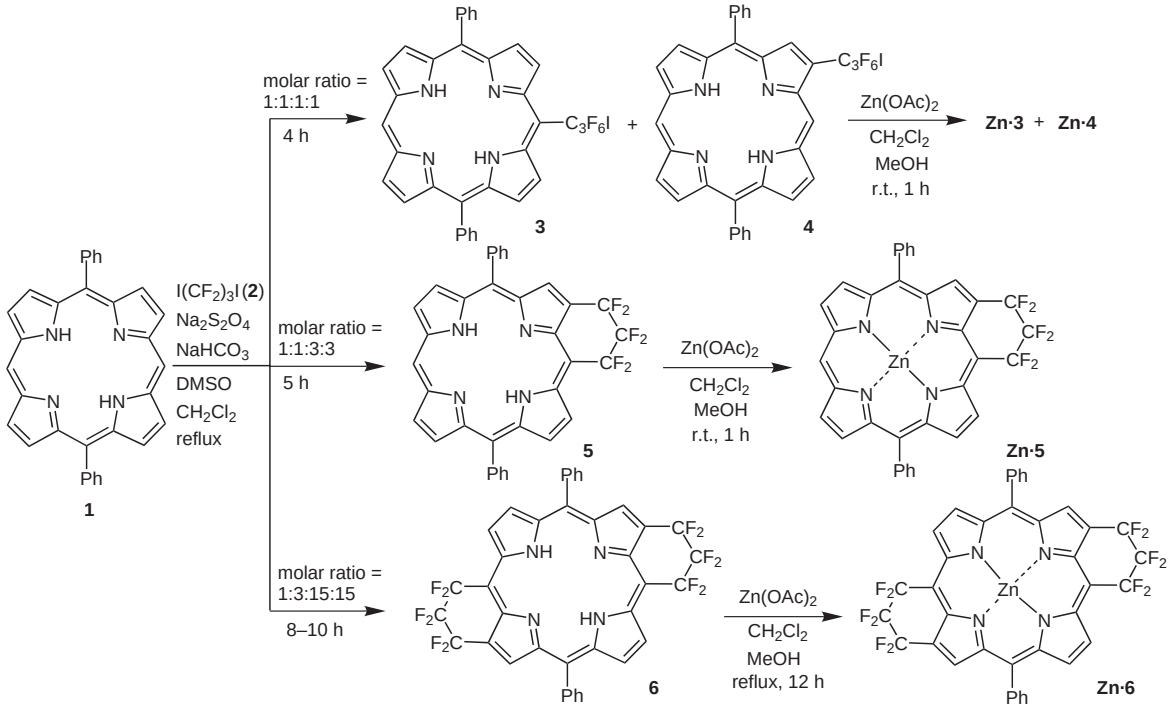
Changing the molar ratio of the reactants to 1:1:3:3 and prolonged the reaction to 5 hours gave a monofluoroalkylated *meso*,β-fused porphyrin **5** (40%) and recovered starting material **1** (45%). Further change of the reactants molar ratio to 1:3:15:15 and a reaction time to 8–10 hours resulted in the formation of a double fluoroalkylated *meso*,β-fused porphyrin **6** (25%) together with recovered **1** (50%).

The metalation capabilities of porphyrins **5** and **6** are different. The 5,15,-diphenyl-2,20-hexafluoropropano-porphyrinatozinc complex (**Zn·5**) could be readily prepared in nearly quantitative yield from the reaction of **5** with $Zn(OAc)_2$ in CH_2Cl_2–MeOH (v/v, 1:1) at room temperature for 1 hour, whereas the double fluoroalkylated fused porphyrin **6** metalated extremely slowly under the same reaction conditions. The zinc complex **Zn·6** was obtained only in 70% conversion in refluxing CH_2Cl_2–MeOH (v/v, 1:1) for 12 hours. This differential complexation ability comes most likely from the diminished basicity of nitrogen in **6** relative to that in **5**, due to the presence of an additional electron-withdrawing $CF_2CF_2CF_2$ group.

The structures of fluoroalkyl-fused porphyrins **3**, **Zn·3**, **4**, **Zn·4**, **5**, **Zn·5**, **6** and **Zn·6** were established by ^1H NMR and ^{19}F NMR spectroscopy, mass spectral and elemental analyses.[10] X-ray crystallographic analyses of **6** and **Zn6** were also performed.[11]

Originally, in sulfinatodehalogenation reaction conditions, $NaHCO_3$ was used to maintain the reaction medium mildly basic in order to prevent the rapid decomposition of $Na_2S_2O_4$.[12] It was found that when the reaction between **1** and **2** was carried out in the absence of $NaHCO_3$ under

SYNLETT 2007, No. 13, pp 2096–2100
Advanced online publication: 12.07.2007
DOI: 10.1055/s-2007-984888; Art ID: W02707ST

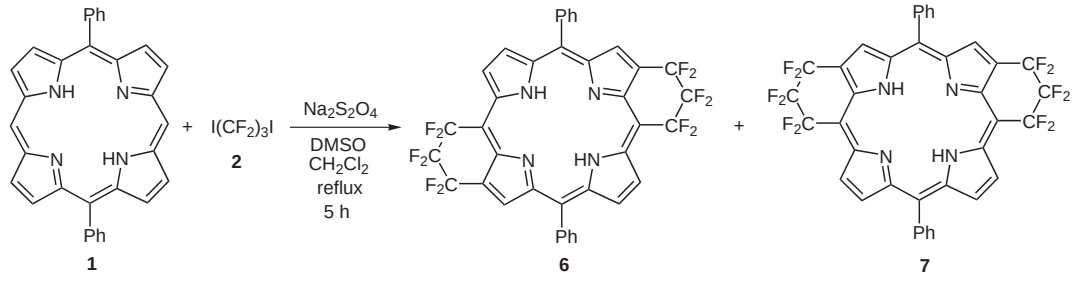


Scheme 1 Reaction of 5,15-diphenylporphyrin with 1,3-diiodohexafluoropropane, $Na_2S_2O_4$/$NaHCO_3$

otherwise identical reaction conditions, the reaction rate was accelerated and finished within 5 hours instead of 12 hours (Scheme 2). After the usual workup, a new compound was isolated which gave the same molecular ion peak as that of compound **6** in the MALDI-MS spectrum. But its ^{1}H NMR spectrum suggested that it was a structural isomer of **6** (i.e. **7**).[13] From ^{1}H NMR integration, the product ratio of **6** to **7** was 1:1. Unfortunately, they could not be separated by chromatography because of their very similar polarities. The formation of **7** may be ascribed to another cyclization pathway of fluorinated porphyrin radical.

The above results obtained with 1,3-diiodohexafluoropropane (**2**) prompted us to extend this approach to other α,ω-chloroiodoperfluoroalkanes so as to investigate the stepwise cyclizations. Recently, we found that reaction of zincated 5,15-diphenylporphyrin with $ClCF_2CF_2I$ gave mono-*meso*-fluoroalkylated porphyrin **Zn·8** and bis-*meso*,*meso*-fluoroalkylated porphyrin **Zn·9** under sulfinatodehalogenation conditions.[14] Using our method for activation of C–Cl bonds in perfluoroalkyl chlorides,[15] the intramolecular cyclization of **Zn·8** proceeded smoothly in DMSO at 120 °C for 5 hours in the presence of $Na_2S_2O_4$/$NaHCO_3$ (reactants molar ratio = 1:10:10) to afford monocyclized 5,10-diphenyl-2,20-(tetrafluoroethanediyl) porphyrinato zinc(II) **Zn·10** (30%) with recovery of **Zn·8** (50%) (Scheme 3). Subsequent demetalation with concentrated HCl yielded the free base porphyrin **10**. The double cyclization of **Zn·9** could also be performed under the same reaction conditions for 8 hours. As expected, two isomers **Zn·11** and **Zn·12** were formed, but their polarities were too close to allow their clean separation. Decreasing the reactant molar ratio to 1:5:5 gave a monofluoroalkylated *meso*,β-fused porphyrin **Zn·13** (40%) and two isomers **Zn·11** and **Zn·12** (10%). The structures of the isomers were assigned on the basis of their ^{1}H NMR and ^{19}F NMR spectra, MALDI-MS. The ^{1}H NMR and ^{19}F NMR spectra showed the isomer distribution was 1:1.3.[16]

A careful analysis of the above results observed with **1**, **Zn·8** and **Zn·9** allowed us to consider that a faster radical cyclization led to lower product regioselectivity. In the absence of $NaHCO_3$, the $Na_2S_2O_4$ would decompose

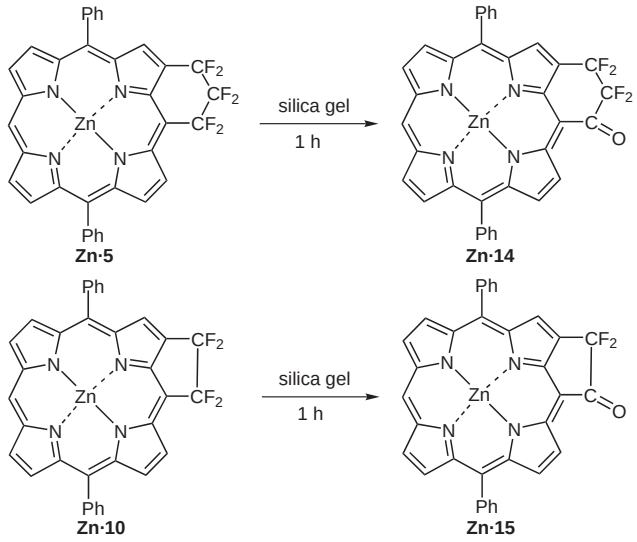


Scheme 2 The reaction of 5,15-diphenylporphyrin with 1,3-diiodohexafluoropropane, $Na_2S_2O_4$

rapidly to produce a higher concentration of fluoroalkyl radicals, which accelerated the cyclization and resulted in a lower selectivity in the reaction of **1** with **2**. To initiate the cyclization of zinc(II) 5,15-bis(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (**Zn·9**), a higher temperature (120 °C) was needed to activate the carbon–chlorine bond. Thus the selectivity was also lowered due to the rapid intramolecular cyclization. The cyclization process might also carry out through the intermediate **Zn·13** in a stepwise manner.

We earlier observed the hydrolysis of a CF_2 moiety in 5,10,15-triaryl-2,20-perfluoroalkanoporphyrinato zinc,[8] the monocyclized porphyrins **Zn·5** and **Zn·10** could also be hydrolyzed by simply treating them with silica gel to give the oxo compounds **Zn·14** and **Zn·15** (Scheme 4).[17] The zincated products were converted into the corresponding free-base porphyrins **14** and **15** quantitatively with concentrated HCl. Unexpectedly, the double cyclized porphyrin **Zn·6** remained intact under the same hydrolysis conditions.

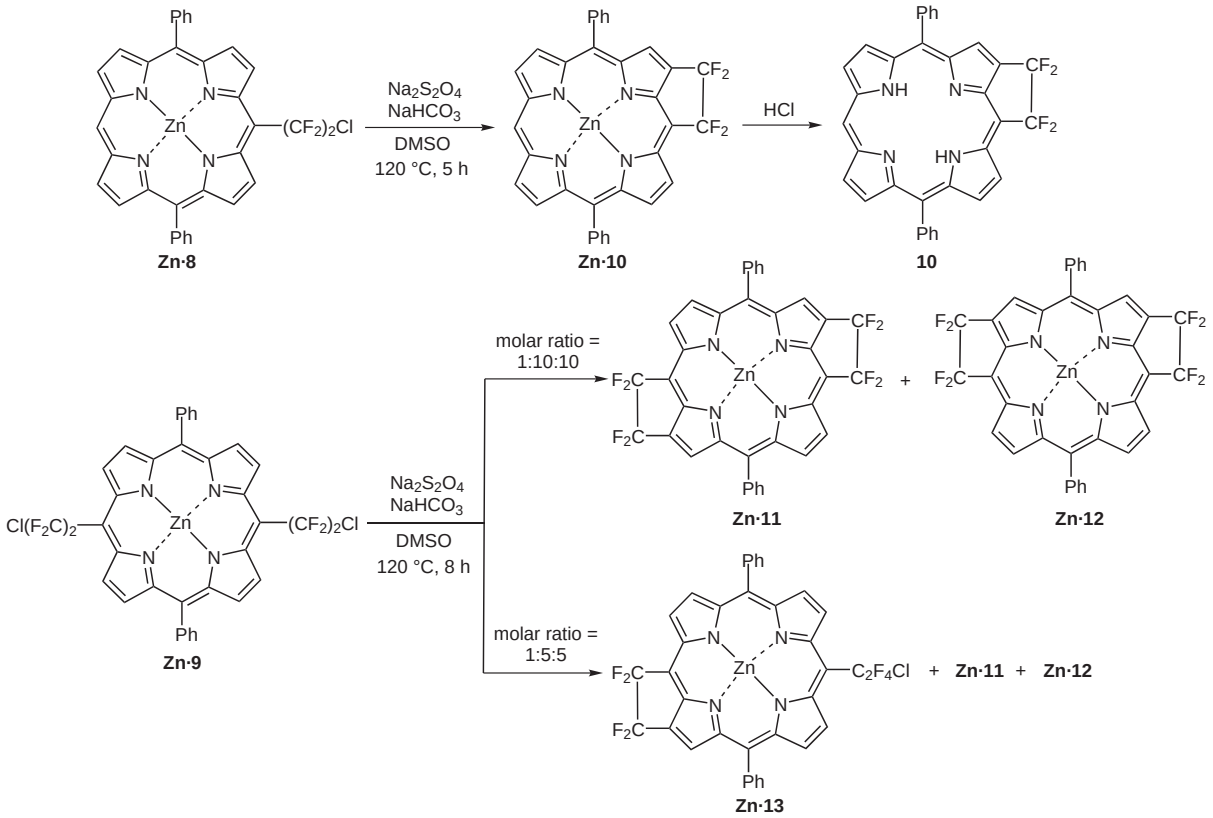
In summary, we have developed for a practical route to the synthesis of double-fluorinated *meso*,β-fused porphyrins by radical cyclization. Furthermore, the two fused rings could be introduced stepwise into the peripheral of the porphyrins. These fluorinated fused porphyrins are expected to be useful in coordination chemistry and molecular recognition studies.



Scheme 4 Hydrolysis of **Zn·5** and **Zn·10**

Acknowledgment

We thank the National Nature Science Foundation of China (D 20032010, 20272076) for financial support of this work.



Scheme 3 Intramolecular cyclization of chlorotetrafluoroalkylated porphyrins **Zn·8** and **Zn·9**

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(10) **Preparation of 5,15-Diphenyl-2,20-(hexafluoropropanediyl)porphyrin (5)**
Porphyrin **1** (0.2 mmol) was dissolved in the mixture of DMSO–CH_2Cl_2 (v/v, 15 mL/15 mL), then $ICF_2CF_2CF_2I$ (0.2 mmol), $Na_2S_2O_4$ (0.6 mmol), and $NaHCO_3$ (0.6 mmol) were added in order. The mixture was stirred for 5 h at 65 °C. The course of the reaction was monitored by TLC. After adding 30 mL of CH_2Cl_2 the mixture was washed with H_2O (3×). The organic layer was dried over anhyd Na_2SO_4 and evaporated to dryness. The crude products were purified by column chromatography, using PE–CH_2Cl_2 (v/v, 4:1) as eluent. The first red-purple band was dug out and washed with CH_2Cl_2 to give **5** (40%). The red-purple band was further purified by flash chromatography [300–400 mesh silica gel, PE–CH_2Cl_2 (v/v, 5:1)] to yield a light-purple solid.
Compound **5**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = –3.36 (br d, *J* = 31.2 Hz, 2 H), 7.78–7.89 (m, 6 H), 8.15–8.22 (m, 4 H), 8.83 (d, *J* = 4.8 Hz, 2 H), 9.04 (d, *J* = 5.4 Hz, 2 H), 9.09 (d, *J* = 4.8 Hz, 1 H), 9.19 (d, *J* = 5.4 Hz, 1 H), 9.28 (d, *J* = 4.8 Hz, 1 H) 9.47 (t, *J* = 2.4 Hz, 1 H), 9.98 (br s, 1 H), 10.08 (s, 1 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –82.03 (br s, 2 F), –104.48 (br s, 2 F), –131.83 (br s, 2 F) ppm. UV/Vis (relative intensity, CH_2Cl_2): λ_{max} = 633 (1.0), 582 (2.3), 514 (5.5), 412 (117.6). MS (MALDI-TOF): *m/z* = 611 [MH^+]. Anal. Calcd for $C_{35}H_{20}H_6N_4$×0.5H_2O: C, 67.85; H, 3.42; N, 9.04. Found: C, 68.05; H, 3.39; N, 8.89.
Preparation of 5,15-Diphenyl-2,20:10,12-di(hexafluoropropanediyl)porphyrin (6)
Porphyrin **1** (0.2 mmol) was dissolved in the mixture of DMSO–CH_2Cl_2 (v/v, 15 mL/15 mL), then $ICF_2CF_2CF_2I$ (0.6 mmol), $Na_2S_2O_4$ (3 mmol), and $NaHCO_3$ (3 mmol) was added in order. The mixture was stirred for 8–10 h at 65 °C. The course of the reaction was monitored by TLC. After adding 30 mL of CH_2Cl_2 the mixture was washed with H_2O (3×). The organic layer was dried over anhyd Na_2SO_4 and evaporated to dryness. The crude products were purified by column chromatography, using PE–CH_2Cl_2 (v/v, 5:1) as eluent. The first red-purple band was dug out and washed with CH_2Cl_2 to give **6** (25%). The red-purple band was further purified by flash chromatography [300–400 mesh silica gel, PE–CH_2Cl_2 (v/v, 10:1)] to yield a light-purple solid.
Compound **6**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = –3.12 (s, 2 H), 7.85–7.93 (m, 6 H), 8.21–8.24 (m, 4 H), 9.25 (d, *J* = 5.4 Hz, 2 H), 9.40 (t, *J* = 2.4 Hz, 2 H), 9.99–10.02 (m, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ =–82.96 (br s, 2 F), –104.97 (br s, 2 F), –131.60 (br s, 2 F) ppm. UV/Vis (relative intensity, CH_2Cl_2): λ_{max} = 640 (1.3), 586 (1.0), 560 (1.3), 521 (1.9), 414 (44.3). MS (MALDI): *m/z* = 759 [MH^+]. HRMS (MALDI): *m/z* calcd for for $C_{38}H_{19}N_4F_{12}^+$: 759.1418; found: 759.1427.

(11) **Crystal Data of 6**
CCDC no. 635096, $C_{38}H_{18}F_{12}N_4$, *MW* = 758.56, *T* = 293 (2) K, *l* = 0.71073 Å, monoclinic, space group *P*2(1)/*c*, *a* = 14.531 (2) Å, *b* = 10.9219 (18) Å, *c* = 10.1624 (17) Å, *α* = 90°, *β* = 95.964 (4)°, *γ* = 90°, *V* = 1604.1 (5) Å^3, *Z* = 2, *D* = 1.571 g/cm^3, *μ* = 0.143 mm^{-1}, *F*(000) = 764, crystal size: 0.365 × 0.332 × 0.130 mm, 9244 reflections collected, 3493 independent reflections [*R*(int) = 0.0660]; refinement method: full-matrix least-squares on F^2; goodness-of-fit on F^2 = 0.920, final *R* indices [I > 2 σ(I)] *R*1 = 0.0627, *wR*2 = 0.1834; *R* indices (all data) *R*1 = 0.1202, *wR*2 = 0.2067.
Crystal Data of 6·Zn
CCDC no. 635097, $C_{38}H_{16}F_{12}N_4Zn$, *MW* = 821.92, *T* = 293 (2) K, *l* = 0.71073 Å, monoclinic, space group *P*2(1)/*c*, *a* = 14.4919 (15) Å, *b* = 11.1408 (12) Å, *c* = 9.9987 (11) Å, *α* = 90°, *β* = 95.509 (2)°, *γ* = 90°, *V* = 1606.8 (3) Å^3, *Z* = 2, *D* = 1.699 g/cm^3, *μ* = 0.872 mm^{-1}, *F*(000) = 820, crystal size: 0.292 × 0.231 × 0.051 mm, 8214 reflections collected, 2987 independent reflections [*R*(int) = 0.0581]; refinement method: full-matrix least-squares on F^2; goodness-of-fit on F^2 = 1.036, final *R* indices [I > 2 σ(I)] *R*1 = 0.0668, *wR*2 = 0.1788; *R* indices (all data) *R*1 = 0.0888, *wR*2 = 0.1937.

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(13) **Mixture of 5,15-Diphenyl-2,20:10,12-di(hexafluoropropanediyl)porphyrin(6) and 5,15-Diphenyl-2,20:8,10-di(hexafluoropropanediyl)porphyrin (7)**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.96 (m, 12 H, **6** + **7**), 8.16–8.25 (m, 8 H, **6** + **7**), 9.03 (d, *J* = 5.4 Hz, 2 H, **7**), 9.25 (d, *J* = 5.4 Hz, 2 H, **6**), 9.40 (t, *J* = 2.4 Hz, 2 H, **6**), 9.45 (t, *J* = 2.4 Hz, 2 H, **7**), 9.80 (s, 2 H, **7**), 9.98–10.02 (m, 2 H, **6**) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –83.07 (br s, 4 F, **6** + **7**), –104.89 (br s, 4 F, **6** + **7**), –131.42 (br s, 4 F, **6** + **7**). MS (MALDI): *m/z* = 759 [MH^+].

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(16) **General Procedure for the Preparation of 5,15-Diphenyl-2,20:10,12-di(tetrafluoroethanediyl)porphinato Zinc(II) (Zn·11) and 5,15-Diphenyl-2,20:8,10-di(tetrafluoroethanediyl)porphinato Zinc(II) (Zn·12)**
Zinc porphyrin **Zn·9** (0.1 mmol) was dissolved in the 20 mL DMSO, then $Na_2S_2O_4$ (1 mmol) and $NaHCO_3$ (1 mmol) were added in order. The mixture was stirred for 8 h at 120 °C. The course of the reaction was monitored by TLC. After adding 40 mL CH_2Cl_2, the mixture was washed with H_2O several times. The organic layer was dried over anhyd Na_2SO_4 and evaporated to dryness. The crude products were purified by flash chromatography [300–400 mesh silica gel, PE–CH_2Cl_2 (v/v, 1:1)], the main purple band was the mixture of **Zn·11** and **Zn·12** (40%). The ratio of two isomers was 1:1.3.
Mixture of 5,15-Diphenyl-2,20:10,12-di(tetrafluoroethanediyl)porphinato Zinc(II) (Zn·11) and 5,15-Diphenyl-2,20:8,10-di(tetrafluoroethanediyl)porphinato Zinc(II) (Zn·12)
^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 7.90–7.95 (m, 13.8 H, **Zn·11** + **Zn·12**), 8.27–8.44 (m, 9.2 H, **Zn·11** + **Zn·12**), 9.13 (d, *J* = 4.2 Hz, 2 H, **Zn·12**), 9.16 (d, *J* = 4.2 Hz, 2.6 H, **Zn·11**), 9.41 (s, 2.6 H, **Zn·11**), 9.47 (s, 2 H, **Zn·12**), 9.64 (d,

J = 4.2 Hz, 2.6 H, **Zn·11**), 9.69 (d, *J* = 4.2 Hz, 2 H, **Zn·12**) ppm. ^{19}F NMR [282 MHz, $(CD_3)_2SO$]: δ = –78.79 (s, 2 F, **Zn·12**), –79.11 (s, 2.6 F, **Zn·11**), –95.31 (s, 2 F, **Zn·12**), –95.80 (s, 2.6 F, **Zn·11**) ppm. UV/Vis (relative intensity, CH_2Cl_2): λ_{max} = 550 (1.0), 416 (30.4). MS (MALDI): *m/z* = 720.1 [M^+]. HRMS (MALDI): *m/z* calcd for for $C_{36}H_{17}N_4F_8Zn^+$: 721.0611; found: 721.0595.

General Procedure for the Preparation of 5,15-Diphenyl-10-(2-chlorotetrafluoroethyl)-2,20-tetrafluoroethanediylporphinato Zinc(II) (Zn·13)

Zinc porphyrin **Zn·9** (0.1 mmol) was dissolved in 20 mL DMSO, then $Na_2S_2O_4$ (0.5 mmol) and $NaHCO_3$ (0.5 mmol) were added in order. The mixture was stirred for 8 h at 120 °C. The course of the reaction was monitored by TLC. After adding 40 mL CH_2Cl_2, the mixture was washed with H_2O several times. The organic layer was dried over anhyd Na_2SO_4 and evaporated to dryness. The crude products were purified by flash chromatography [300–400 mesh silica gel, PE–CH_2Cl_2 (v/v, 1:1)]. The first red-purple band was **Zn·13** (40%). The second red-purple band was the mixture of **Zn·11** and **Zn·12** (10%).

5,15-Diphenyl-10-(2-chlorotetrafluoroethyl)-2,20-tetrafluoroethanediylporphinato Zinc(II) (Zn·13)

^{1}H NMR [300 MHz, $(CD_3)_2SO$]: δ = 7.85–7.92 (m, 6 H,), 8.22–8.29 (m, 4 H), 8.97 (d, *J* = 4.8 Hz, 1 H), 9.03 (d, *J* = 4.8 Hz, 1 H), 9.07 (d, 1 H), 9.23 (d, *J* = 1.8, 1 H), 9.61 (d, *J* = 4.8Hz, 1 H), 9.64 (s, 1 H) ppm. ^{19}F NMR [282 MHz, $(CD_3)_2SO$]: δ = –62.98 (s, 2 F), –72.56 (s, 2 F), –79.93 (br s, 2 F), –95.36 (br s, 2 F) ppm. UV/Vis (relative intensity, CH_2Cl_2): λ_{max} = 553 (1.0), 416 (30.1). MS (MALDI): *m/z* = 756.0 [M^+]. HRMS (MALDI): *m/z* calcd for for $C_{36}H_{18}N_4F_8ClZn^+$: 757.0378; found: 757.0351.

(17) **Hydrolysis of 5,15-Diphenyl-2,20-(hexafluoropropanediyl)porphinato Zinc(II) (Zn·5) and 5,15-Diphenyl-2,20-(tetrafluoroethanediyl)porphinato Zinc(II) (Zn·10)**

A sample of **Zn·5** or **Zn·10** (15 mg) was dissolved in 10 mL CH_2Cl_2, then silica gel (300–400 mesh) was added. The solvent was evaporated to dryness. The powder was exposed to air for 1 h, then directly subjected to chromatography (silica, CH_2Cl_2). The green band was collected to yield **Zn·14** or **Zn·15**.

5,15-Diphenyl-2,20-(20′-oxo)-(tetrafluoropropanediyl) porphinato Zinc(II) (Zn·14)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.88 (m, 6 H), 8.14–8.22 (m, 4 H), 8.92 (d, *J* = 4.2 Hz, 1 H), 8.95 (d, *J* = 4.8 Hz, 1 H), 9.05 (d, *J* = 4.8 Hz, 1 H), 9.28 (d, *J* = 1.8 Hz, 1 H), 9.29 (d, *J* = 1.8 Hz, 1 H), 9.52 (s, 1 H), 10.21 (s, 1 H), 10.31 (d, *J* = 4.8 Hz, 1 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –102.20 (t, *J* = 13.0 Hz, 2 F, β-CF_2), –121.58 (t, *J* = 13.8 Hz, 2 F, CF_2CO) ppm. UV/Vis (relative intensity, CH_2Cl_2): λ_{max} = 607 (2.0), 561 (1.0), 426 (29.8). IR (KBr): 1637 (C=O) cm^{-1}. MS (MALDI): *m/z* = 650 [M^+]. Anal. Calcd for $C_{35}H_{18}F_4N_4OZn$: C, 64.48; H, 2.78; N, 8.59. Found: C, 64.47; H, 3.06; N, 8.34.