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Rational Synthesis of *meso*- or *β*- Fluoroalkylporphyrin Derivatives via Halo-fluoroalkylporphyrin Precursors: Electronic and Steric Effects on Regioselective Electrophilic Substitution in 5-Fluoroalkyl-10,20-diarylporphyrins

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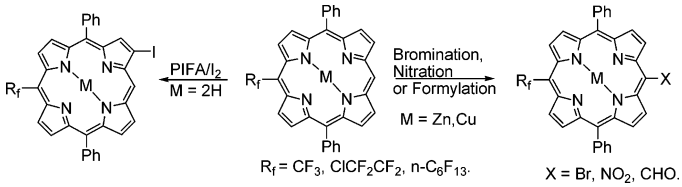

Electrophilic nitration, formylation or bromination of metalated 5-fluoroalkyl-10,20-diphenylporphyrin (fluoroalkyl = CF_3, $ClCF_2CF_2$, *n*-C_6F_{13}) proceeded with high regioselectivity, exclusively affording corresponding meso-substituted porphyrins, while the iodination reaction mainly took place at the adjacent *β* site giving 2-iodo-10-fluoroalkyl-5,15-diphenylporphyrin. Suzuki, Sonogashira, and trifluoromethylation reactions of the obtained 5-bromo-15-fluoroalkyl-10,20-diphenylporphyrins or 2-iodo-10-fluoroalkyl-5,15-diphenylporphyrins could perform smoothly to give the corresponding various meso- or *β*-functionalized fluoroalkylated porphyrin derivatives. Accordingly, two meso-to-meso butadiyne-bridged bisporphyrin dimers and two *β*-to-*β* butadiyne-linked dimeric porphyrins were prepared by the coupling reactions of 5-ethynyl-15-fluoroalkyl-10,20-diphenylporphyrins and 2-ethynyl-10-fluoroalkyl-5,15-diphenylporphyrins, respectively.

Introduction

Per(poly)fluoroalkylporphyrins and their metallic complexes have been shown to possess unique properties in catalysis, materials, and medical applications et cetera.[1] For example, DiMagno and co-workers have shown that the 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin ligand was successfully used as a fluorocarbon-soluble sensitizer for the photooxidation of allylic alcohols to hydroperoxide under a fluorous biphase system.[2] Pandey and colleagues have found that the fluorinated porphyrins, as compared with the corresponding nonfluorinated analogues, generally have higher PDT efficacy.[3] The existing elegant procedures for the synthesis of symmetric fluoroalkylporphyrins are usually almost all variations on the same theme,

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that is, the condensation of fluoroalkylpyrroles and fluoroalkylaldehydes under acidic conditions.[4] Recently, we found that a modified sulfinatodehalogenation system ($Na_2S_2O_4$/$NaHCO_3$/DMSO) or metal (e.g., copper powder) was suitable for synthesizing the symmetrical and asymmetrical fluoroalkylporphyrins from easily available synthetic porphyrins and commercial per(poly)fluoroalkyl iodides (R_fI).[5] For example, treatment of tetraarylporphyrins/R_fI with $Na_2S_2O_4$ or copper powder afforded the mono β-fluoroalkylporphyrins in moderate to good yields.[5a−c] Similarly, fluoroalkylation of 5,15-diarylporphyrins under sulfinatodehalogenation conditions provided an access to prepare both mono-, meso-, and β-fluoroalkylated porphyrins.[5e] Because of the relatively large size and high electron deficiency of the fluoroalkyl group, the resultant 5-fluoroalkyl-10,20-diarylporphyrins, as compared with other 5,10,15-triarylporphyrins, would be expected to display some interesting characteristics in regioselective electrophilic substitution reactions. Herein we present the results.

Results and Discussion

1. Electrophilic Substitution of 5-Fluoroalkyl-10,20-diphenylporphyrins. To gain insight into the reactivity of the mono meso fluoroalkylated porphyrins, some electrophilic substitutions, such as nitration, formylation, bromination, and iodination, were investigated.

The treatment of 5-perfluorohexyl-10,20-diphenylporphinatocopper(II) (**Cu1c**)[5e] with 4 equiv of $Cu(NO_3)_2$/Ac_2O (acetic anhydride)[6] at 30 °C for 24 h, followed by demetalation with H_2SO_4, resulted in meso-NO_2-substituted compound **2** exclusively with no corresponding β-NO_2-substituted product being detected. Similarly, following the standard formylation procedure,[7] 5-(2-chlorotetrafluoroethyl)-10,20-diphenylporphinatocopper(II) (**Cu1b**)[5e] or **Cu1c** reacted with DMF/$POCl_3$ in 1,2-dichloroethane at 50 °C for 12h, followed by hydrolysis with saturated NaOAc (aq), and then demetalation with H_2SO_4 afforded meso-formylated porphyrins **3b** and **3c** respectively. The ^{1}H NMR spectrum showed no formation of a β-CHO-substituted product. As expected, treating 5-triflurometyl-10,20-diphenylporphinatozinc(II) (**Zn1a**),[8] 5-(2-chlorotetrafluoroethyl)-10,20-diphenylporphinatozinc(II) (**Zn1b**)[5e] or 5-perfluorohexyl-10,20-diphenylporphinatozinc(II) (**Zn1c**)[5e] with 1.1 equiv of *N*-bromosuccimimide (NBS) in dichloromethane at room temperature for 10 min resulted in the formation of corresponding meso-brominated products **Zn4a**, **Zn4b**, and **Zn4c** with high regioselectivity, respectively. While NBS reacted with corresponding free base porphyrins, for example, 5-perfluorohexyl-10,20-diphenylporphyrin (**1c**),[5e] the main meso bromoporphyrin (70%) along with a small amount of β-bromoporphyrin (20%), as determined by the ^{1}H NMR spectrum, was obtained. Contrary to the high meso-site selectivity of nitration, formylation, and bromination, the iodination of free base **1c** with 1.1 equiv of phenyliodide bistrifluoroacetate (PIFA)/I_2, according to Dolphin's method,[9] mainly afforded β-iodoporphyrin **5c** with only a small amount of *meso*-iodoporphyrin **5 cm** (Scheme 1).[10] The molar ratio of the two isomers, determined by ^{1}H NMR spectra, was about 7:1; moreover, they could be separated by long column chromatography despite their close polarity. Furthermore, the ^{1}H NMR spectra of such compounds are quite distinctive and indicative of their structures. As shown in Figure 1A, the ^{1}H NMR spectrum of compound **5c** illustrates the formation of the β-iodinated product. In the meso-proton region, only one meso-proton resonance is present (10.3 ppm). Seven different sets of β-hydrogen resonances are observed between 8.0 and 10.0, and among them, the β-proton adjacent to the iodine shows clearly a singlet at 9.01 ppm, and the singlet at −2.90 ppm belongs to the N−H proton resonance. Because of its symmetric structure, *meso*-iodoporphyrin **5cm** gives a relatively simple ^{1}H NMR spectrum: only four sets of doublet resonances are exhibited in the β-proton region. Notably, its N−H-proton resonance peak is split into a doublet (−2.35, −2.45 ppm).

The position of iodine in compound **5c** was further confirmed by NOESY (Figure 2). The fact that no correlation peak of the protons of H^3 and H^{20} can be found in the NOESY spectrum indicated that iodine was attached at the 2 position of the macrocycle. Similar results were also obtained from the iodination of 5-trifluoromethyl-10,20-diphenylporphyrin (**1a**)[8] and 5-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (**1b**)[5e] (Experimental Section). This is similar to that of the fluoroalkylation of 5-fluoroalkyl-10,20-diphenylporphyrins. The second fluoroalkyl group was introduced onto the meso and β positions in almost equal yield.[5e] However, for other meso-triaryl-substituted porphyrins, for example, iodination or fluoroalkylation of the free-base triarylporphyrins, the iodine or the fluoroalkyl group was mainly attached to the remaining meso position.[5d,11]

As seen in Table 1,[12] the fluoroalkyl groups (CF_3, *n*-C_6F_{13}, etc.) are substantially larger than phenyl, so the fluoroalkylated macrocycles become more compressed compared to 5,10,15-triphenylporphyrin. Additionally, iodination is more sensitive to steric effects than other reactions, such as formylation, nitration, and bromination, etc., because iodine has the highest

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(10) When the corresponding zincated porphyrins were used as starting materials, meso, meso linked bisporphyrins were exclusively formed. For details about the synthesis of such meso, meso linked bisporphyrins, see ref 8.

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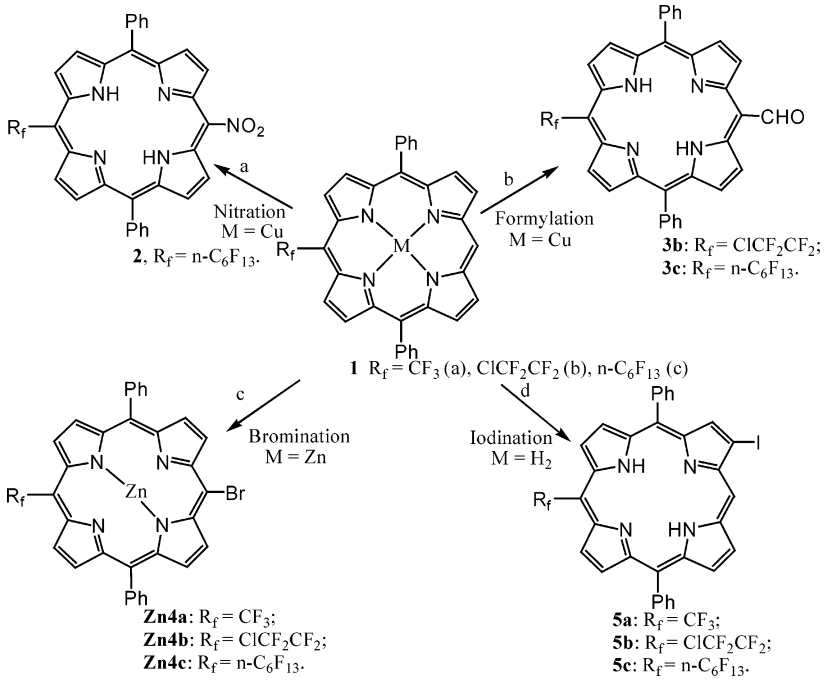
SCHEME 1. Some Electrophilic Reactions of Fluoroalkylporphyrins[a]



[a] Reagents and conditions: (a) (i) $Cu(NO_2)_2$, AcOH, Ac_2O, 35 °C, 24 h; (ii) H_2SO_4, rt, 5 min, total yield: 80%. (b) (i) DMF/$POCl_3$, CH_2Cl_2, reflux, 12 h; (ii) NaOAc(aq), 75 °C, 1 h; (iii) H_2SO_4, CH_2Cl_2, rt, 30 min, total yield: 90−95%. (c) NBS, CH_2Cl_2, rt, 1 h, 90−95%. (d) I_2, PIFA, CH_2Cl_2, 1 h, 60−70%.

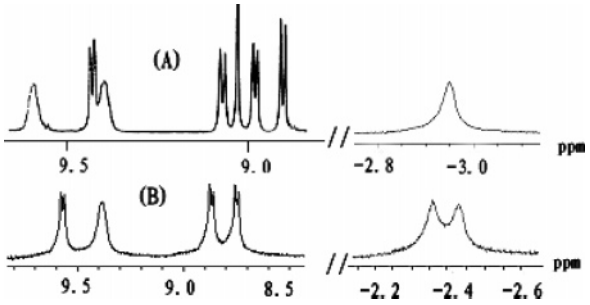


FIGURE 1. ^{1}H NMR spectra of β-iodofluoroalkylporphyrin **5c** (A, only β proton and N−H proton peaks are shown) and *meso*-iodofluoroalkylporphyrin **5cm** (B, only β proton and N−H proton peaks are shown).

steric constant among the substituents (NO_2, Br, I). Thus, it is understandable that iodine was mainly attached to the less steric position, namely, the 2 position of the porphyrins in the above iodination reactions. These results are also consistent with Dolphin's observations of further iodination of 5-iodo-10,20-diphenylporphyrin.[13]

2. Transformation of Regio-haloporphyrins. Halogenated porphyrins are one type of very useful precursors for synthesizing porphyrin derivatives otherwise inaccessible. Many elegant metal-mediated methods have been developed for functionalizing porphyrins from bromo and iodoporphyrin precursors.[14] But such transformations are all limited to the meso positions probably because halogenation has only taken place at the meso position for 5,10,15-triarylporphyrins. As mentioned above, we have successfully developed high regioselective halogenation at the meso and β positions of 5-fluoroalkyl-10,20-diphenylporphyrins. The different regioselective halogenated porphyrins obtained would be expected to provide useful precursors for synthesizing various regional-functional-porphyrin derivatives and new kinds of push−pull chromorphores.

The meso-halogenated bromo and iodoporphyrins under standard trifluoromethylation conditions[15] could be smoothly converted into corresponding meso trifluoromethylated porphyrins. Thus, treatment of zincated *meso*-bromo-fluoroalkylporphyrin **Zn4a** and **Zn4b** with 10 equiv of $FSO_2CF_2CO_2Me$ in DMF at 100 °C in the presence of 10 equiv of CuI for 2 h resulted in corresponding trifluoromethylated products **6a** and **6b** in ∼80% yield. Meanwhile, following standard Sonogashira reaction conditions,[16] treating **Zn4b** or **Zn4c** with 5 equiv of HC≡C−R in the presence of 10 mol % $Pd(PPh_3)Cl_2$ and CuI in THF and triethylamine(TEA) at room temperature for 2h afforded green pigment **7** in >90% yield (Scheme 2).

To evaluate the reactivity of 2-iodo-10-fluoroalkyl-5,15-diphenylporphyrins, trifluoromethylation, Sonogashira, and Suzuki reactions were also investigated. For example, treatment of zincated β-iodoporphyrin **Zn5b** (M = Zn, R_f = ClC_2F_4−) with 10 equiv of $FSO_2CF_2CO_2Me$ in DMF at 100 °C in the presence of 10 equiv of CuI for 1 h, followed by demetalation with 36% HCl resulted in β-trifluoromethylated product **8b** in

(13) Dolphin observed in the iodination of 5,15-diphenylporphyrin that 1.5 equiv of bis(trifluoroacetoxy)iodobenzene-iodine (1.2:1) gave monoiodo-5,15-diphenylporphyrin in yields greater than 70% after separation from the contaminating diiodo-5,15-diphenylporphyrin. NMR examination of the two iodination products revealed that whereas the first iodination takes place at one of the two available meso positions the second substitution occurs not at the remaining meso position but indiscriminately at a β position resulting in a mixture of regioisomers.[9]

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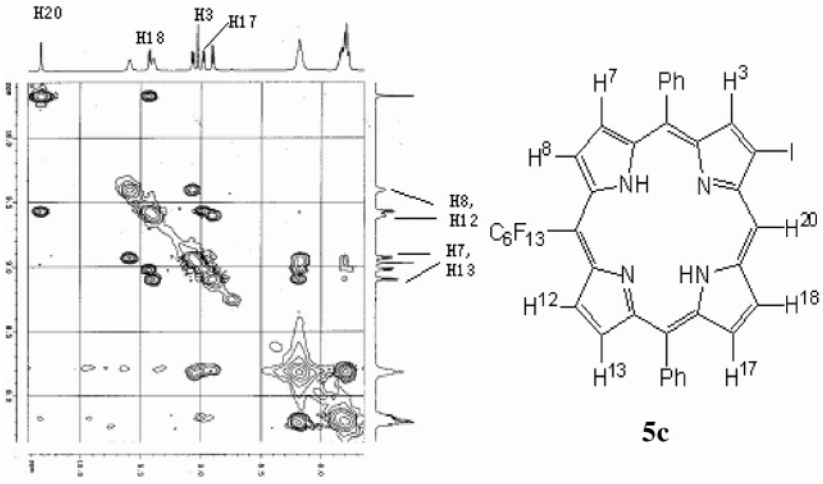

FIGURE 2. NOSEY spectrum of **5c**. (Only the aromatic region is shown.)

TABLE 1. Steric Constants for the Substituents

no.	substituent	*Es*[a]
1	H	0.00
2	C_6H_5	−1.01
3	NO_2	−1.01
4	Br	−1.16
5	CF_3	−2.40
6	I	−1.40

[a] *Es* is the steric constant defined by Taft from ref 12.

90% yield. Both Sonogashira and Suzuki reactions[17] were also readily performed. Namely, compound **10** was easily obtained in >90% yield by the reaction of the zincated β-iodoporphyrin with HC≡C−R. Mixing the free base of β-iodoporphyrin **5c** (M = H_2, R_f = C_6F_{13}−) with $PhB(OH)_2$ in the presence of 10 mol % $Pd(PPh_3)_4$ and K_2CO_3 in toluene at 100 °C for 2 h afforded compound **9** in 90% yield (Scheme 3).

3. Synthesis of meso, meso- or β, β-Butadiyne-Linked Bis(fluoroalkylporphyrins). With the *meso*- and β-trimethylsilylethynyl substituted porphyrins in hand, some further transformations were carried out. After desilylation with $(n\text{-Bu})_4NF$, the resulting ethynylporphyrins **11, 12** could couple in the presence of $PdCl_2(PPh_3)_2$/CuI/air to produce meso-to-meso and β-to-β butadiyne-linked bisporphyrins **13** and **14** in high yield, respectively (Scheme 4). The UV−visible and fluorescence spectra of such bisporphyrins are shown in Figure 3. As seen in Figure 3, both compounds **Zn13b** and **Zn14b** exhibit B-band-region absorptions that span a near-constant window of the solar spectrum (400−550 nm), though their respective Soret regions that are strongly dependent on the nature of porphyrin-to-porphyrin connectivity. The wavelength of the lowest-energy $\pi-\pi^*$ transition displays a similar relationship to butadiynyl bridging topology: altering the mode of connectivity for the butadiyne from meso-to-meso to β-to-β results in a shift of the lowest-energy Q-type transition from 694.0 to 607.0 nm. The same phenomenon was also observed in the emission spectrum. The meso-to-meso linked-bisporphyrin dimer **Zn13b** exhibits an emission band at 700.0 nm, which is a longer wavelength than that observed for the fluorescence emission of the less electronically coupled, β-to-β linked dimeric porphyrin **Zn14b** (616.5 nm). Similar results have been observed previously in corresponding butadiynyl-bridged nonfluorinated porphyrins by Therien and co-workers.[18]

In conclusion, the electrophilic aromatic substitution reactions, such as formylation, nitration, and bromination of 5-fluoroalkyl-10,20-diphenylporphyrin and its metalated derivatives, mainly take place at the remaining meso position, whereas iodination occurs primarily at the β site. Several simple procedures of regioselective syntheses of various meso- and β-functionalized fluoroalkylporphyrins from corresponding halogenated precursors have also been demonstrated. Among these, the first direct access to porphyrins bearing a trans arrangement (5,15) of perfluoroalkyl and alkyne functional groups is presented. These substitution patterns are expected to be useful in building new alkyne-linked arrays with interesting properties.

Experimental Section

Nitration of Copper(II) 5-Perfluorohexyl-10,20-diphenylporphyrin (Cu1c). $Cu(NO_3)_2 \cdot 3H_2O$ (45 mg) in Ac_2O (4.5 mL) was added to **Cu1c** (80 mg) dissolved in a mixture of $CHCl_3$ (75 mL) and acetic acid (1.5 mL). The reaction mixture was stirred at room temperature for 24 h, and TLC (petroleum ether/CH_2Cl_2 = 3:1) showed no starting material. The solution was subsequently washed with water and aqueous K_2CO_3 and dried over Na_2SO_4. The organic layer was treated with H_2SO_4 (0.5 mL) at room temperature for 30 min and then washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was purified by flash chromatography (silica gel, 300−400 mesh, petroleum ether/CH_2Cl_2 = 5:1). The main band was collected and evaporated to dryness to give purple solid **2** (63 mg, 80%, recrystallized from $CHCl_3$−methanol).

5-Nitro-15-(perfluorohexyl)-10,20-diphenylporphyrin (2). ^1H NMR ($CDCl_3$, 300 MHz) δ: 9.49 (m, 2H), 9.32 (d, J = 4.9 Hz, 2H), 8.94 (t, J = 5.4 Hz, 4H), 8.16 (d, J = 7.2 Hz, 4H), 7.85−7.76 (m, 6H), −2.87 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −75.57 (m, 2F), −76.80 (t, J = 9 Hz, 3F), −111.20 (m, 2F), −117.17 (m, 2F), −118.50 (m, 2F), −122.05 (m, 2F). MS(MALDI) *m*/*z*: 826.6 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 415 (5.32), 514 (4.14), 556 (4.13), 590 (3.88), 650 (4.08). Anal. calcd for $C_{38}H_{20}F_{13}N_5O_2$: C, 55.28; H, 2.44; N, 8.48; found: C, 55.30; H, 2.82; N, 8.27.

Formylation of Copper(II) 5-Fluoroalkyl-10,20-diphenylporphyrins. DMF (0.3 mL) was cooled to 5−10 °C, $POCl_3$ (0.4 mL) was added under N_2, and the mixture was stirred for 15 min. The ice bath was removed, and the solution was stirred for another 15

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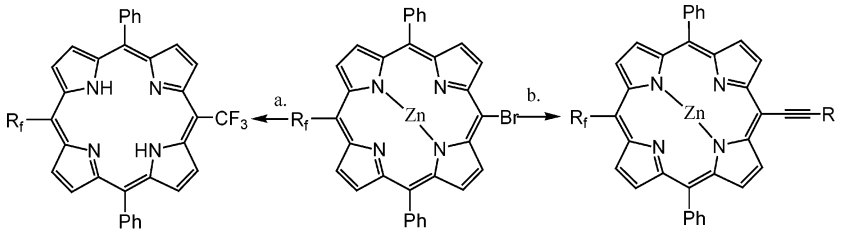
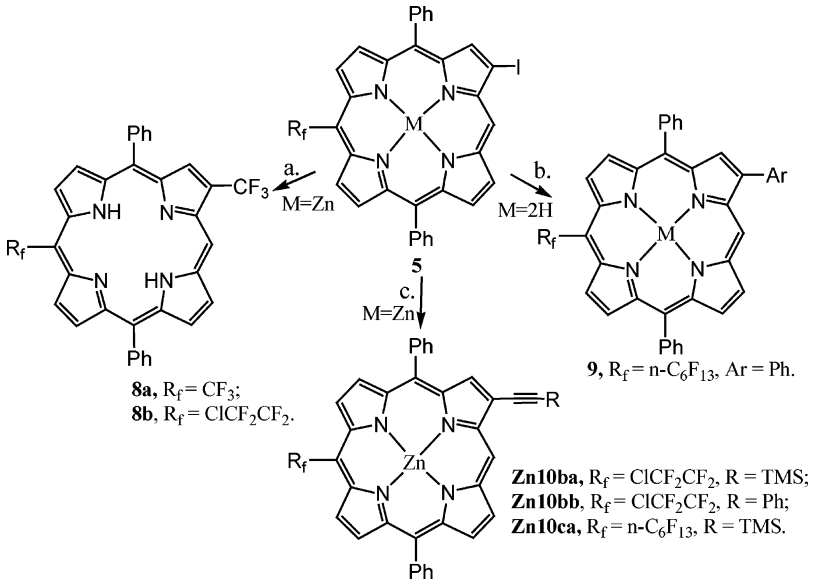
SCHEME 2. Transformation of meso-Halogenated Porphyrins[a]



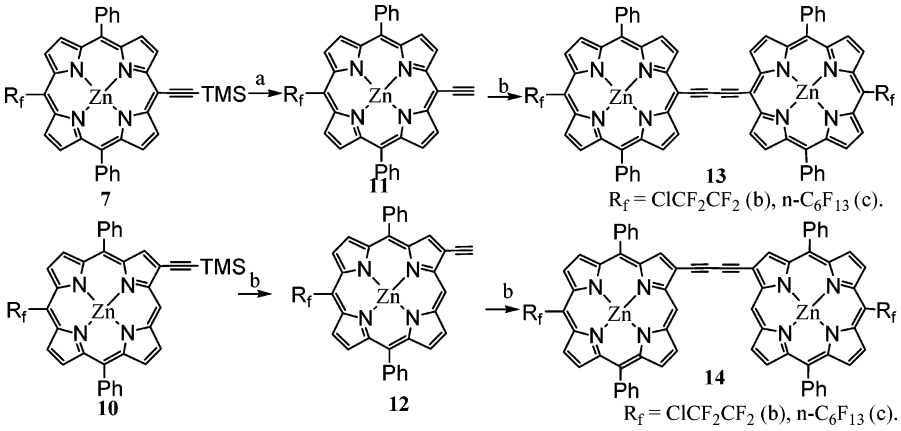
[a] Reagents and conditions: (a) (i) $FSO_2CF_2CO_2Me$, CuI, DMF, 100 °C, 2 h; (ii) concd HCl, 10 min, 80%. (b) Alkyne, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, rt, 2 h, 90−95%.

SCHEME 3. Some Transformations of *β*-Iodinated Porphyrins[a]



[a] Reagents and conditions: (a) (i) $FSO_2CF_2CO_2Me$, CuI, DMF, 100 °C, 2 h; (ii) HCl (36% aq), 90%. (b) $PhB(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, toluene, 100 °C, 4 h, 90%. (c) Alkyne, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, rt, 2 h, 95%.

SCHEME 4. Synthesis of Butadiyne-Linked Bis(fluoroalkylporphyrin)[a]



[a] Reagents and conditions: (a) $(n\text{-}Bu)_4NF$, THF, rt 1 h, quantitative. (b) $PdCl_2(PPh_3)_2$, CuI, air, Et_3N, THF, rt, 30 min, 93−97%.

min. Dry dichloromethane (5 mL) was then added, and the reagent was cooled to 0−5 °C. This solution was added dropwise to a solution of **Cu1b** (100 mg, 0.152 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred at 45 °C overnight. Then a saturated solution of NaOAc (40 mL) was added, and the mixture was stirred at 70 °C for 1 h, after which the organic phase was separated, washed with water, and dried over Na_2SO_4, and the solvent was evaporated. Column chromatography on silica (CH_2Cl_2/hexanes, 1:2) afforded **Cu3b** (99 mg, 95%). The treatment of a solution of **Cu3b** (50 mg, 0.073 mmol) in CH_2Cl_2 (50 mL) with H_2SO_4 (0.2 mL) at room

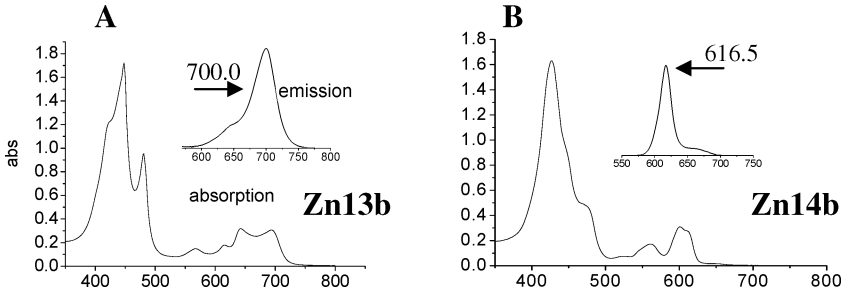


FIGURE 3. Electronic absorption and fluorescene emission spectra of butadiyne-bridged bisporphyrins **Zn13b** (A) and **Zn14b** (B) in THF solution (c = 6.9925 μM) at room temperature.

temperature for 30 min, following the preliminary workup (wash with water, remove solvent by rotary evaporation), resulted in **3b** quantitatively.

Copper(II) 5-Formyl-15-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (Cu3b). MS(MALDI) *m/z*: 685.1 ([M]$^+$). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 418 (9), 561 (0.3), 607 (1). HRMS(MALDI) calcd for $C_{35}H_{19}N_4OF_4{}^{35}Cl^{63}Cu$: 685.0474; found: 685.0491.

5-Formyl-15-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (3b). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 12.49 (s, 1H), 10.03 (d, J = 4.7 Hz, 2H), 9.50 (m, 2H), 8.98 (d, J = 5.1 Hz, 2H), 8.88 (d, J = 5.5 Hz, 2H), 8.17 (d, J = 7.0 Hz, 4H), 7.82 (m, 6H), −2.33 (s, 1H), −2.43 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −64.33 (s, 2F), −79.28 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ:194.3, 148.3, 146.9, 145.9, 145.0, 141.8, 140.7, 140.6, 138.6, 134.5, 134.4, 134.4, 134.2, 133.4, 131.1, 128.9, 128.5, 128.44, 128.37, 128.30, 127.1, 126.9, 126.8, 125.3, 122.9, 109.7. MS(ESI) *m/z*: 626.15 ([M + 2]$^+$). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 420 (13), 525 (0.5), 568 (1.1), 608 (0.3), 664 (1). HRMS(MALDI) calcd for $C_{35}H_{21}N_4OF_4{}^{35}Cl\cdot H^+$: 625.1413; found: 625.1448.

Copper(II) 5-Formyl-15-(perfluorohexyl)-10,20-diphenylporphyrin (Cu3c). Similarly, the reaction of **Cu1c** (64 mg, 0.076 mmol) with DMF (0.15 mL) and $POCl_3$ (0.2 mL) and purification by column chromatography on silica (CH_2Cl_2/hexanes, 1:2) afforded **Cu3c** (60 mg, 90%).

MS(ESI) *m/z*: 870.20 (MH$^+$). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 418 (5.55), 558 (4.06), 604 (4.52). HRMS(MALDI) calcd for $C_{39}H_{19}N_4OF_{13}{}^{63}Cu$: 869.0642; found: 869.0667.

5-Formyl-15-(perfluorohexyl)-10,20-diphenylporphyrin (3c). The title compound was obtained quantitatively from **Cu3c** by treating it with H_2SO_4.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 12.51 (s, 1H), 10.04 (d, J = 4.8 Hz, 2H), 9.47 (m, 2H), 8.99 (d, J = 5.1 Hz, 2H), 8.89 (d, J = 5.6 Hz, 2H), 8.19−8.15 (m, 4H), 7.86−7.77 (m, 6H), −2.35 (s, 1H), −2.45 (s, 1H).^{19}F NMR ($CDCl_3$, 282 MHz) δ: −81.3 (m, 2F), −81.7 (m, 3F), −116.1 (m, 2F), −121.8 (m, 2F), −123.3 (m, 2F), −125.8 (m, 2F). MS(ESI) *m/z*: 809.25 (MH$^+$). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 418(13), 524(0.5), 566(1.1), 664(1). HRMS(MALDI) calcd for $C_{39}H_{21}N_4OF_13\cdot H^+$: 809.1581; found: 809.1581.

Bromination of Zinc(II) 5-Fluoroalkyl-10,20-diphenylporphyrins. A sample of **Zn1a** (50 mg, 0.084 mmol) and NBS (16 mg, 0.09 mmol) was stirred in $CHCl_3$ (50 mL) and pyridine (0.1 mL) at room temperature for 10 min. The resulting mixture was washed with water, dried over Na_2SO_4, and evaporated to yield a purple solid. ^{19}F and ^{1}H NMR analysis of the crude products indicated no formation of the β-brominated product. Recrystalization from CH_2Cl_2/hexanes yielded **Zn4a** (53 mg, 95%).

Zinc(II) 5-Bromo-15-trifluoromethyl-10,20-diphenylporphyrin (Zn4a). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 9.66 (d, J = 4.7 Hz, 2H), 9.58−9.53 (m, 2H), 8.84 (d, J = 5.3 Hz, 2H), 8.75 (d, J = 5.0 Hz, 2H), 8.17−8.14 (m, 4H), 7.87−7.79 (m, 6H). ^{19}F NMR (DMSO-d_6, 282 MHz) δ: −33.16 (t, J = 3.0 Hz, 3F). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 151.35, 149.53, 148.99, 148.97, 148.80, 142.30, 134.62, 134.50, 133.93, 133.24, 130.68 (q, J_{C-F} = 7 Hz), 128.42, 127.25, 122.91, 108.14. MS(MALDI) *m/z*: 670.0 (M$^+$). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 421 (46), 555 (2.1), 589 (1). HRMS(MALDI) calcd for $C_{33}H_{18}N_4F_3{}^{79}Br^{65}Zn$: 669.9953; found: 669.9963.

Zinc(II) 5-Bromo-15-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (Zn4b). Similarly, the title compound was obtained from the reaction of **Zn1b** (30 mg, 0.045 mmol) and NBS (9 mg, 0.05 mmol) in 90% yield (30 mg).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.55 (d, J = 3.8 Hz, 4H), 8.91 (d, J = 4.1 Hz, 2H), 8.76 (d, J = 3.8 Hz, 2H), 8.09 (m, 4H), 7.75 (m, 6H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.09 (s, 2F), −74.83 (s, 2F). MS(MALDI) *m/z*: 736.0 (M$^+$). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 419 (36), 552 (1.6), 584 (1). HRMS(MALDI) calcd for $C_{34}H_{18}N_4F_4{}^{35}Cl^{79}Br^{65}Zn\cdot H^+$: 736.9704; found: 736.9674.

Zinc(II)5-Bromo-15-perfluorohexyl-10,20-diphenylporphyrin (Zn4c). The title compound was obtained from the reaction of **Zn1c** (30 mg, 0.035 mmol) and NBS (7 mg, 0.039 mmol) in 90% yield (29 mg).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.68 (d, J = 4.5 Hz, 2H), 9.46 (m, 2H), 8.91 (d, J = 4.8 Hz, 2H), 8.82 (d, J = 4.8 Hz, 2H), 8.20−8.10 (m, 4H), 7.79−7.71(m, 6H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −76.59 (m, 2F), −81.02 (t, J = 10.8 Hz, 3F), −115.14 (m, 2F), −121.45 (m, 2F), −122.79 (m, 2F), −126.31 (m, 2F). MS(MALDI) *m/z*: 920.0 (M$^+$). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 418 (5.62), 551 (4.25), 584 (4.06). HRMS(MALDI) calcd for $C_{38}H_{18}N_4{}^{65}ZnF_{13}{}^{79}Br$: 919.9793; found: 919.9770.

Iodination of 5-Fluoroalkyl-10,20-diphenylporphyrins. A sample of **1a** (100 mg, 0.19 mmol), I_2 (28 mg, 0.11 mmol), and PIFA (47 mg, 0.11 mmol) was stirred in CH_2Cl_2 (50 mL) at room temperature for 1 h. The resulting mixture was washed with saturated $Na_2S_2O_3$ solution, dried over Na_2SO_4, and evaporated to yield a purple solid. ^{19}F and ^{1}H NMR analysis of the crude products indicated about a 1:6 product ratio (meso-iodinated porphyrin versus β-iodinated porphyrin). The obtained residue was further purified by chromatography (silica gel, 300−400 mesh, CH_2Cl_2/hexanes = 1:20 by vol), and the main band was collected to give **5a** (84 mg, 68%).

2-Iodo-10-trifluoromethyl-5,15-diphenylporphyrin (5a). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.34 (s, 1H), 9.76 (m, 1H), 9.55 (m, 1H), 9.45 (d, J = 4.8 Hz, 1H), 9.09 (d, J = 5.2 Hz, 1H), 9.06 (s, 1H), 9.01 (d, J = 4.3 Hz, 1H), 8.92 (d, J = 4.7 Hz, 1H), 8.23−8.18 (m, 4H), 7.84−7.81 (m, 6H), −2.91 (s, 2H).^{19}F NMR ($CDCl_3$, 282 MHz) δ: −35.41(s, 3F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ:141.62, 141.37, 141.16, 140.97, 135.60, 134.50, 134.43, 132.21, 131.32, 130.80, 130.34, 129.43, 129.19, 128.26, 128.17, 126.97, 126.91, 121.36, 120.40, 108.31. MS(ESI) *m/z*: 657.25(MH$^+$). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 413 (107), 511 (7.6), 545 (2.6), 582 (2.8), 637 (1). Anal. calcd for $C_{33}H_{20}F_{13}IN_4\cdot 0.5H_2O$: C, 59.56; H, 3.18; N, 8.44; found: C, 59.59; H, 3.70; N, 8.82.

2-Iodo-10-(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (5b). The title compound was obtained from the reaction of **1b**(100 mg, 0.17 mmol), I_2(22 mg, 0.09 mmol), and PIFA (37 mg, 0.09 mmol) in 60% yield (74 mg).

^{1}H NMR ($CDCl_3$, 300 MHz) δ:10.28 (s, 1H), 9.62 (m, 1H), 9.43 (m, 1H), 9.39 (d, J = 4.6 Hz, 1H), 9.04 (d, J = 5.1 Hz, 1H), 9.00 (s, 1H), 8.95 (d, J = 4.3 Hz, 1H), 8.87 (d, J = 5.1 Hz, 1H), 8.17−8.14 (m, 4H), 7.83−7.74 (m, 6H), −2.97 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −64.08 (s, 2F), −77.18 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 141.76, 141.72, 141.47, 135.75, 134.42, 134.36, 131.46, 129.33, 128.29, 128.17, 126.91, 126.84, 121.18, 120.47, 108.37. MS(ESI) *m*/*z*: 723.05 (MH^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 413 (5.39), 512 (4.2), 546 (3.77), 582 (3.78), 6.36 (3.48). Anal. calcd for $C_{34}H_{20}ClF_4IN_4$: C, 56.49; H, 2.79; N, 7.75; found: C, 56.06; H, 3.14; N, 7.40.

Zinc(II) 2-Iodo-10-(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (Zn5b). Treating **5b** (30 mg, 0.04 mmol) with $Zn(OAc)_2$ (91 mg, 0.4 mmol) in CH_2Cl_2 (30 mL)/CH_3OH (5 mL) at room temperature for 1 h, following the preliminary workup (wash with water, remove solvent by rotary evaporation), resulted in **Zn5b** quantitatively.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.97 (s, 1H), 9.66−9.63 (m, 2H), 9.12 (s, 1H), 9.10 (d, J = 4.8 Hz, 1H), 9.04 (d, J = 3.5 Hz, 1H), 9.02 (d, J = 4.8 Hz, 1H), 8.81(d, J = 4.3 Hz, 1H), 8.17−8.11 (m, 4H), 7.85−7.77 (m, 6H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.07 (s, 2F), −74.44 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.41, 150.77, 150.41, 150.33, 149.63, 149.10, 148.83, 147.66, 142.13, 141.95, 139.69, 134.37, 134.33, 133.93, 133.01, 132.41, 132.08, 127.99, 127.87, 126.77, 126.70, 121.89, 120.89, 108.94, 93.19. MS(MALDI) *m*/*z*: 784.0 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 414 (5.54), 544 (4.18), 577 (4.08). HRMS(MALDI) calcd for $C_{34}H_{18}{}^{35}ClF_4IN_4{}^{65}Zn$: 783.9487; found: 783.9520.

2-Iodo-10-perfluorohexyl-5,15-diphenylporphyrin (5c) and 5-Iodo-10-perfluorohexyl-5,15-diphenylporphyrin (5cm). A sample of **1c** (100 mg, 0.13 mmol), I_2 (19 mg, 0.07 mmol), and PIFA (30 mg, 0.07 mmol) were stirred in CH_2Cl_2 (50 mL) at room temperature for 1 h. The resulting mixture was washed with saturated $Na_2S_2O_3$ solution, dried over Na_2SO_4, and evaporated to yield a purple solid. ^{19}F and ^{1}H NMR analysis of the crude products indicated about a 1:7 product molar ratio (meso-iodinated porphyrin versus β-iodinated porphyrin). The obtained residue was further purified by chromatography (silica gel, 300−400 mesh, CH_2Cl_2/hexanes = 1:20 by vol) to produce two bands. The first band resulted in **5cm** (12 mg, 10%), and the second main band resulted in **5c** (82 mg, 70%).

5cm: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.57 (d, J = 4.5 Hz, 2H), 9.38 (m, 2H), 8.87 (d, J = 5.0 Hz, 2H), 8.75 (d, J = 4.1 Hz, 2H), 8.17−8.09 (m, 4H), 7.82−7.76 (m, 6H), −2.37 (s, 1H), −2.43 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −80.26 (m, 2F), −80.74 (m, 3F), −115.43 (m, 2F), −121.14 (m, 2F), −122.47 (m, 2F), −126.02 (m, 2F). MS(MALDI) *m*/*z*: 907.3 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 419 (5.38), 518 (4.12), 553 (3.98), 592 (3.68), 649 (3.75). Anal. calcd for $C_{38}H_{20}F_{13}IN_4$: C, 50.35; H, 2.22; N, 6.18; found: C, 50.22; H, 2.82; N, 5.73.

5c: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.33 (s, 1H), 9.59 (m, 1H), 9.44 (d, J = 4.4 Hz, 1H), 9.37 (m, 1H), 9.06 (d, J = 5.3 Hz, 1H), 9.02 (s, 1H), 8.98 (d, J = 5.1 Hz, 1H), 8.89 (d, J = 4.7 Hz, 1H), 8.18−8.16 (m, 4H), 7.84−7.75 (m, 6H), −2.94 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.84 (m, 2F), 81.08 (m, 3F), −115.62 (m, 2F), −121.45 (m, 2F), −122.77 (m, 2F), −126.32 (m, 2F). MS(MALDI) *m*/*z*: 907.3 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 414 (5.47), 512 (4.30), 547 (3.97), 581 (3.93), 636 (3.65). Anal. calcd for $C_{38}H_{20}F_{13}IN_4$: C, 50.35; H, 2.22; N, 6.18; found: C, 50.34; H, 2.91; N,5.84.

Zinc(II) 2-Iodo-10-perfluorohexyl-5,15-diphenylporphyrin (Zn5c). The title compound was obtained by the reaction of **5c** (50 mg, 0.055 mmol) and $Zn(OAc)_2$ (121 mg, 0.55 mmol) in CH_2Cl_2 (50 mL)/CH_3OH (5 mL) quantitatively.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.24 (s, 1H), 9.57 (m, 2H), 9.34 (d, J = 4.6 Hz, 1H), 9.17 (s, 1H), 9.05 (d, J = 5.0 Hz, 1H), 9.04 (d, J = 5.2 Hz, 1H), 8.94 (d, J = 4.6 Hz, 1H), 8.16−8.14 (m, 4H), 7.84−7.76 (m, 6H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −76.20 (m, 2F), −80.57 (m, 3F), −114.62 (m, 2F), −120.92 (m, 2F), −122.28 (m, 2F), −125.80 (m, 2F). MS(MALDI) *m*/*z*: 968.0 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 414 (28), 544 (1.2), 576 (1). HRMS(MALDI) *m*/*z*: calcd for $C_{38}H_{18}N_4F_{13}I^{65}Zn$: 967.9655; found: 967.9646.

Reactions of Zinc(II) 5-Bromo-15-fluoroalkyl-10,20-diphenylporphyrins. Trifluoromethylation of Zn4. A sample of **Zn4a** (30 mg, 0.044 mmol) was treated with excess $FSO_2CF_2CO_2Me$ (26 μL, 0.44 mmol) and CuI (90 mg, 0.44 mmol) in DMF (3 mL) and HMPA (3 mL) at 100 °C for 8 h. After the mixture was cooled to room temperature, CH_2Cl_2 (50 mL) was added, and the mixture was washed with water. The organic phase was separated and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford a purple solid. The crude product was dissolved in CH_2Cl_2, treated with concentrated HCl (1 mL) at room temperature for 10 min, and then washed with water and purified by column chromatography (300−400 mesh silica, CH_2Cl_2/hexanes (1:10)) to give **6a** (21 mg, 80%).

5,15-Bis(trifluoromethyl)-10,20-diphenylporphyrin (6a). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.61 (m, 4H), 8.92 (d, J = 5 Hz, 4H), 8.16 (m, 4H), 7.81 (m, 6H), −2.65 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −37.3 (s, 6F). MS(MALDI) *m*/*z*: 599.1 (MH^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 410 (24), 512 (1.3), 547 (1.2), 590 (0.6), 644 (1). HRMS(MALDI) calcd for $C_{34}H_{20}N_4F_6{\cdot}H^+$: 599.1665; found: 599.1671.

5-Trifluoromethyl-15-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (6b). Similarly, following the general procedure for the synthesis of **6a**, the reaction of **Zn4b** (40 mg, 0.054 mmol) with $FSO_2CF_2CO_2Me$ (32 μL, 0.54 mmol) and CuI (110 mg, 0.54 mmol) and demetalation with 36% HCl afforded **6b** (28 mg, 80%).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.61 (m, 2H), 9.52 (m, 2H), 8.91 (d, J = 5.2 Hz, 4H), 8.17 (d, J = 6.8 Hz, 4H), 7.80 (m, 6H), −2.50 (s, 1H), −2.63 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −37.2 (m, 3F), −64.01 (s, 2F), −79.29 (s, 2F). MS(MALDI) *m*/*z*: 664.1 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 410 (21), 511 (1.1), 547 (1.1), 591 (0.5), 645 (1). HRMS(MALDI) calcd for $C_{35}H_{20}N_4F_7{}^{35}Cl{\cdot}H^+$: 665.1338; found: 665.1347.

Typical Procedure for Sonogashira Coupling Reaction between Zn4 and Alkynes. Zinc(II) 5-Trifluoromethyl-15-phenylethynyl-10,20-diphenylporphyrin (Zn7ab). A mixture of **Zn4a** (30 mg, 0.044 mmol), $Pd(PPh_3)_2Cl_2$ (4 mg), CuI (2 mg), 1-ethynylbenzene (44 mg, 0.44 mmol), and triethylamine (4.5 mL) was stirred in THF (30 mL) at room temperature under N_2 for 2 h. The resulting greenish solution was evaporated to dryness, and the residue was purified by flash chromatography (silica gel, CH_2Cl_2/hexanes, 1:1) to afford **Zn7ab** (29 mg, 95%).

^{1}H NMR (DMSO-d_6, 300 MHz) δ: 9.82 (d, J = 4.8 Hz, 2H), 9.57−9.54 (m, 2H), 8.84 (d, J = 5.1 Hz, 2H), 8.81 (d, J = 4.8 Hz, 2H), 8.19−8.13 (m, 6H), 7.86−7.83 (m, 6H), 7.65−7.60 (m, 3H). ^{19}F NMR (DMSO-d_6, 282 MHz) δ: −33.54 (s, 3F). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 151.15, 150.55, 149.64, 148.21, 142.32, 134.60, 134.16, 132.97, 132.15, 132.11, 130.69, 130.52, 129.72, 129.57, 128.43, 127.30, 123.41, 123.19, 103.05, 97.64, 92.63. MS(MALDI) *m*/*z*: 692.1 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 435 (14), 566 (0.6), 609 (1). HRMS(MALDI) calcd for $C_{41}H_{23}N_4F_3{}^{65}Zn$: 692.1161; found: 692.1185.

Zinc(II) 5-(2-Chlorotetrafluoroethyl)-15-trimethylsilylethynyl-10,20-diphenylporphyrin (Zn7ba). Similarly, following the general procedure for the synthesis of **Zn7ab**, the reaction of **Zn4b** (40 mg, 0.054 mmol) with ethynyltrimethylsilane (54 mg, 0.54 mmol) afforded **Zn7ba** (39 mg, 93%). Demetalation with 36% HCl resulted in corresponding free base **7ba** quantitatively.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.72 (d, J = 4.3 Hz, 2H), 9.61 (m, 2H), 8.99 (d, J = 4.9 Hz, 2H), 8.89 (d, J = 4.3 Hz, 2H), 8.18 (d, J = 6.2 Hz, 4H), 7.81 (m, 6H), 0.66 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.37 (s, 2F), −75.26 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.6, 150.8, 149.9, 149.6, 142.9, 142.4, 134.4, 133.6, 132.6, 132.0, 131.9, 131.8, 129.8, 128.1, 127.8, 126.6, 122.6, 122.4, 107.1, 102.9, 102.8, 0.4. MS(MALDI) *m*/*z*: 754.1 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 428 (18), 562 (0.7), 602 (1).

HRMS(MALDI) calcd for $C_{39}H_{27}N_4F_4{}^{35}ClSi^{65}Zn\cdot H^+$: 755.0994; found: 755.0966. Anal. calcd for $C_{39}H_{27}N_4F_4ClSiZn\cdot 0.5H_2O$: C, 61.18; H, 3.69; N, 7.32; found: C, 61.49; H, 4.14; N, 6.5.

5-(2-Chlorotetrafluoroethyl)-15-trimethylsilylethynyl-10,20-diphenylporphyrin (7ba). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.61 (d, J = 4.8 Hz, 2H), 9.46 (m, 2H), 8.88 (d, J = 5.1 Hz, 2H), 8.81 (d, J = 4.3 Hz, 2H), 8.18−8.16 (m, 4H), 7.84−7.77 (m, 6H), 0.62 (s, 9H), −2.40 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −64.19 (s, 2F), −78.34 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 141.92, 134.32, 133.43, 130.58, 128.16, 126.77, 122.00, 105.83, 104.09, 0.25. MS-(MALDI) m/z: 692.2 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 422 (5.23), 525 (3.97), 564 (4.15), 602 (3.65), 659 (3.89). HRMS-(MALDI) calcd for $C_{39}H_{30}N_4F_4{}^{35}ClSi$: 693.1859; found: 693.1840.

Zinc(II) 5-(2-Chlorotetrafluoroethyl)-15-phenylethynyl-10,20-diphenylporphyrin (Zn7bb). Similarly, following the general procedure for the synthesis of **Zn7ab**, the reaction of **Zn4b** (48 mg, 0.065 mmol) with 1-ethynylbenzene (66 mg, 0.65 mmol) afforded **Zn7bb** (46 mg, 95%).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.76 (d, J = 4.8 Hz, 2H), 9.56 (m, 2H), 8.95 (d, J = 5.0 Hz, 2H), 8.89 (d, J = 4.5 Hz, 2H), 8.18 (d, J = 6.4 Hz, 4H), 7.98 (d, J = 6.9 Hz, 2H), 7.80 (m, 6H), 7.50 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.45 (s, 2F), −75.3 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.3, 150.6, 150.1, 150.0, 149.5, 142.4, 134.6, 134.3, 133.6, 132.5, 132.1, 131.9, 131.8, 131.7, 131.6, 128.7, 127.8, 126.6, 123.8, 122.6, 97.3, 92.1. MS(MALDI) m/z: 758.1 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 436 (14), 567 (0.6), 620 (1). HRMS(MALDI) calcd for $C_{42}H_{23}N_4{}^{65}ZnF_4$-Cl: 758.0833; found: 758.0878.

Zinc(II) 5-Perfluorohexyl-15-trimethylsilylethynyl-10,20-diphenylporphyrin (Zn7ca). Similarly, the reaction of **Zn4c** (50 mg, 0.054 mmol) with ethynyltrimethylsilane (54 mg, 0.54 mmol) afforded **Zn7ca** (48 mg, 95%).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.69 (d, J = 4.1 Hz, 2H), 9.45 (m, 2H), 8.90 (d, J = 5.1 Hz, 2H), 8.85 (d, J = 4.9 Hz, 2H), 8.17−8.07 (m, 4H), 7.80−7.73 (m, 6H), 0.61 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −76.7 (m, 2F), −81.02 (t, J = 9.7 Hz, 3F), −115.16 (m, 2F), −121.50 (m, 2F), −122.74 (m, 2F), −125.31 (m, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.72, 150.90, 150.04, 149.59, 142.15, 134.30, 133.79, 132.70, 131.98, 131.76, 131.69, 127.93, 126.70, 122.79, 106.78, 103.46, 0.27. MS(MALDI) m/z: 938.1 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 427 (16), 561 (0.6), 601 (1). HRMS(MALDI) calcd for $C_{43}H_{27}N_4{}^{65}ZnF_{13}Si$: 938.1083; found: 938.1078.

Reactions from 2-Iodo-10-fluoroalkyl-5,15-diphenylporphyrin. Trifluoromethylation of Zinc(II) 2-Iodo-10-fluoroalkyl-5,15-diphenylporphyrins. A sample of **Zn5a** (30 mg, 0.042 mmol) was treated with $FSO_2CF_2CO_2Me$ (25 μL, 0.42 mmol) and CuI (90 mg, 0.42 mmol) in DMF (5 mL) at 100 °C for 2 h. After the mixture was cooled to room temperature, CH_2Cl_2 (50 mL) was added, and the mixture was washed with water. The organic phase was separated and dried (Na_2SO_4). The residue was dissolved in 30 mL of CH_2Cl_2, and then 0.5 mL of HCl (36%) was added. The mixture was stirred at room temperature for 10 min and then washed with water, and the solvent was removed under reduced pressure to afford a purple solid, which was recrystallized from CH_2Cl_2/CH_3OH to give **8a** (23 mg, 90%).

2,10-Bis(trifluoromethyl)-5,15-diphenylporphyrin (8a). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.44 (s, 1H), 9.75 (m, 2H), 9.39 (d, J = 4.7 Hz, 1H), 9.27 (s, 1H), 9.08 (m, 2H), 8.98 (d, J = 4.9 Hz, 1H), 8.18 (t, J = 7.5 Hz, 4H), 7.82 (m, 6H), −2.9 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −35.74 (s, 3F), −52.94 (s, 3F). MS-(MALDI) m/z: 599.1 (MH^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 411 (77), 511 (4), 547 (1.7), 583 (1.7), 638 (1). HRMS-(MALDI) calcd for $C_{34}H_{20}N_4F_6\cdot H^+$: 599.1665; found: 599.1677.

2-Trifluoromethyl-10-(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (8b). The title compound was obtained by the reaction of **Zn5b** (30 mg, 0.038 mmol) with $FSO_2CF_2CO_2Me$ (22 μL, 0.38 mmol) and CuI (77 mg, 0.38 mmol), followed by demetalation with HCl (36%) in 90% yield (25 mg). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.45 (s, 1H), 9.63 (m, 1H), 9.46 (d, J = 4.9 Hz, 2H), 9.12 (s, 1H), 9.08 (d, J = 5.3 Hz, 1H), 9.00 (d, J = 4.9 Hz, 1H), 8.90 (d, J = 5.1 Hz, 1H), 8.20 (d, J = 6.8 Hz, 4H), 7.82 (m, 6H), −2.88 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −52.64 (m, 3F), −63.68 (s, 2F), −76.82 (s, 2F). MS(MALDI) m/z: 664.1 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 410 (76), 511 (4.1), 547 (1.8), 582 (1.6), 638 (1). Anal. calcd for $C_{35}H_{20}ClF_7N_4\cdot 2CH_3OH$: C, 60.20; H, 4.22; N, 7.39; found: C, 60.52; H, 4.41; N, 7.25.

Suzuki Reaction of 5c. A mixture of **5c** (50 mg, 0.055 mmol), $Pd(PPh_3)_4$ (4 mg), KCO_3 (2 mg), and $PhB(OH)_2$ (33 mg, 0.28 mmol) was stirred in toluene (40 mL) at 80 °C under N_2 for 2 h. The resulting solution was evaporated to dryness, and the residue was purified by flash chromatography (300−400 mesh silica gel, CH_2-Cl_2/pentane, 1:10) to afford **9** (42 mg, 90%).

5-Perfluorohexyl-10,13,20-triphenylporphyrin (9). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.35 (s, 1H), 9.50 (m, 2H), 9.28 (d, J = 4.2 Hz, 1H), 9.00 (d, J = 5.8 Hz, 1H), 8.98 (s, 1H), 8.90 (d, J = 5.8 Hz, 2H), 8.24 (d, J = 7.4 Hz, 5H), 7.80−7.67 (m, 10H), −2.81 (s, 2H).^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.80 (m, 2F), −81.03 (m, 3F), −115.37 (m, 2F), −121.38 (m, 2F), −122.72 (m, 2F), −126.26 (m, 2F). MS(MALDI) m/z: 857.35 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 637 (3.68), 582 (3.93), 545 (3.98), 510 (4.29), 414 (5.48). Anal. calcd for $C_{44}H_{25}F_{13}N_4$: C, 61.68; H, 2.92; N, 6.54; found: C, 61.88; H, 3.15; N, 6.33.

Sonogashira Coupling Reaction of Zn5. A mixture of **Zn5b** (50 mg, 0.06 mmol), $Pd(PPh_3)_2Cl_2$ (4 mg), CuI (2 mg), ethynyltrimethylsilane (60 mg, 0.6 mmol), and triethylamine (4 mL) was stirred in THF (40 mL) at room temperature under N_2 for 2 h. The resulting light brown solution was evaporated to dryness, and the residue was purified by flash chromatography (300−400 mesh silica gel, THF/pentane, 1:20) to afford **Zn10ba** (43 mg, 95%). Demetalation with concentrated HCl afforded the corresponding free base **10ba** quantitatively.

Zinc(II) 2-Trimethylsilylethynyl-10-(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (Zn10ba). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.45 (s, 1H), 9.61 (m, 2H), 9.39 (d, J = 4.5 Hz, 1H), 9.07 (s, 1H), 9.02 (d, J = 4.8 Hz, 2H), 8.94 (d, J = 4.6 Hz, 1H), 8.19−8.15 (m, 4H), 7.84−7.74 (m, 6H), 0.57 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.09 (s, 2F), −74.39 (s, 2F).^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.75, 150.49, 149.71, 149.17, 149.12, 148.71, 142.45, 142.25, 134.90, 134.40, 134.35, 133.91, 133.77, 133.15, 132.48, 127.86, 127.77, 127.69, 126.67, 126.65, 126.22, 126.20, 121.89, 121.54, 106.92, 103.80, 100.17, 0.201. MS(MALDI) m/z: 754.1 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 418 (5.67), 548 (4.32), 582 (4.36). HRMS(MALDI) calcd for $C_{39}H_{27}N_4F_4{}^{35}ClSi^{65}Zn$: 754.0916; found: 754.0911.

2-Trimethylsilylethynyl-10-(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (10ba). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.51 (s, 1H), 9.63 (m, 2H), 9.47 (d, J = 4.0 Hz, 1H), 9.07 (d, J = 4.9 Hz, 1H), 9.00 (d, J = 4.2 Hz, 1H), 8.96 (s, 1H), 8.91 (d, J = 5.0 Hz, 1H), 8.23−8.18 (m, 4H), 7.85−7.77 (m, 6H), 0.57 (s, 9H), −2.86 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.94 (m, 2F), −77.0 (m, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 141.79, 141.55, 136.76, 135.48, 134.44, 134.38, 131.54, 129.64, 128.24, 128.16, 126.90, 126.86, 121.34, 120.94, 106.18, 104.38, 99.90, 0.32. MS-(MALDI) m/z: 692.2 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 417 (5.44), 515 (4.34), 551 (4.13), 587 (4.02), 641 (3.80). HRMS-(MALDI) calcd for $C_{39}H_{30}N_4F_4{}^{35}ClSi$: 693.1859; found: 693.1842.

Zinc(II) 2-Phenylethynyl-10-(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (Zn10bb). Similarly, the reaction of **Zn5b** (50 mg, 0.06 mmol) with 1-ethynylbenzene (60 mg, 0.6 mmol) afforded **Zn10bb** (43 mg, 95%).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.53 (s, 1H), 9.61 (m, 2H), 9.39 (d, J = 4.5 Hz, 1H), 9.10 (s, 1H), 9.02 (m, 2H), 8.94 (d, J = 3.9 Hz, 1H), 8.20 (m, 4H), 7.91 (d, J = 7.2 Hz, 2H), 7.79 (m, 6H), 7.49 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.38 (s, 2F), −74.59 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.7, 150.5, 149.7, 149.5, 149.2, 148.6, 142.6, 142.4, 134.4, 134.1, 133.7, 132.9, 132.4, 131.9, 131.8, 131.6, 131.4, 128.7, 128.6, 127.8, 127.7, 126.7, 126.6,

126.3, 123.6, 121.8, 121.5, 106.9, 98.0, 84.9. MS(MALDI) *m*/*z*: 758.0895 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 424 (15), 553 (0.8), 587 (1). HRMS(MALDI) calcd for $C_{42}H_{23}N_4{}^{65}ZnF_4{}^{35}Cl$: 758.0833; found: 758.0865.

Zinc(II) 2-Trimethylsilylethynyl-10-perfuorohexyl-5,15-diphenylporphyrin (Zn10ca). Similarly, the reaction of **Zn5c** (50 mg, 0.052 mmol) with ethynyltrimethylsilane (52 mg, 0.52 mmol) afforded **Zn10ca** (46 mg, 95%). The corresponding free base **10ca** was obtained quantitatively by demetalation with concentrated HCl(aq).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.46 (s, 1H), 9.67−9.64 (m, 2H), 9.40 (d, J = 4.5 Hz, 1H), 9.10 (s, 1H), 9.07 (d, J = 5.0 Hz, 1H), 9.06 (d, J = 5.3 Hz, 1H), 8.97 (d, J = 4.5 Hz, 1H), 8.21−8.17 (m, 4H), 7.86−7.77 (m, 6H), 0.59 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −76.82 (s, 2F), −81.02 (s, 2F), −115.11 (s, 2F), −121.38 (s, 2F), −122.71 (s, 2F), −126.25 (s 2F). MS(MALDI) *m*/*z*: 938.1 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 418 (5.67), 548 (4.32), 582 (4.36). HRMS(MALDI) calcd for $C_{43}H_{27}N_4F_{13}Si^{65}Zn$: 938.1083; found: 938.1078.

2-Trimethylsilylethynyl-10-perfuorohexyl-5,15-diphenylporphyrin (10ca). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.45 (s, 1H), 9.57 (m,1H), 9.45 (d, J = 4.8 Hz, 1H), 9.40 (m, 1H), 9.05 (d, J = 5.0 Hz, 1H), 8.98 (d, J = 4.9 Hz, 1H), 8.94 (s, 1H), 8.90 (d, J = 5.0 Hz, 1H), 8.22−8.16 (m, 4H), 7.84−7.76 (m, 6H), 0.56 (s, 9H), −2.82 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −78.6 (m, 2F), −80.88 (t, J = 10.3 Hz, 3F), −115.2 (m, 2F), −121.2 (m, 2F), −122.5 (m, 2F), −126.1 (m, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 141.73, 141.49, 136.53, 135.45, 134.41, 134.34, 131.63, 129.67, 128.28, 128.22, 128.14, 126.88, 126.84, 121.38, 121.03, 106.30, 104.39, 99.86, 0.26. MS(MALDI) *m*/*z*: 877.2 (M^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 417 (64), 515 (4.5), 551 (2.6), 585 (2), 639 (1). HRMS(MALDI) calcd for: $C_{43}H_{30}N_4F_{13}Si$: 877.2027; found: 877.2005.

Synthesis of meso-to-meso and β-to-β Butadiyne-Linked Bisporphyrins. Desilylation of Zn7 and Zn10. To a solution of **Zn7ba** (50 mg, 0.066 mmol) in CH_2Cl_2 (30 mL), a solution of (*n*-Bu)$_4$NF (1 M, 1 mL, in THF) was added. The mixture was stirred at room temperature for 30 min, then water (30 mL) was added, and the reaction mixture was stirred at room temperature for another 30 min. The organic layer was separated, evaporated to dryness, and then recrystallized from CH_2Cl_2/petane to afford **Zn11b** (40 mg, 90%).

Zinc(II) 5-Ethynyl-15-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (Zn11b). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.72 (d, J = 4.5 Hz, 2H), 9.61 (m, 2H), 8.99 (d, J = 4.6 Hz, 2H), 8.92 (d, J = 4.3 Hz, 2H), 8.17 (d, J = 6.0 Hz, 4H), 7.82−7.74 (m, 6H), 4.16 (s, 1H). ^{19}F NMR ($CDCl_3$) δ: −63.49 (s, 2F), −75.28 (s, 2F). MS(MALDI) *m*/*z*: 682.1 (M^+). UV−vis λ_{max} (log ϵ, THF): 426 (5.35), 565 (4.04), 602 (4.1). HRMS(MALDI) calcd for $C_{36}H_{19}N_4F_4{}^{35}Cl^{65}Zn$: 682.0520; found: 682.0519.

5-Ethynyl-15-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (11b). The title compound was obtained quantitatively by demetalation of **Zn11b** with concentrated HCl(aq).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.63 (d, J = 5.2 Hz, 2H), 9.48 (m, 2H), 8.89 (d, J = 5.1 Hz, 2H), 8.83 (d, J = 4.9 Hz, 2H), 8.17 (d, J = 6.6 Hz, 4H), 7.84−7.76 (m, 6H), 4.24 (s, 1H), −2.49 (brs, 2H).^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.48 (s, 2F), −75.29 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 141.91, 134.29, 133.43, 132.31, 130.80, 130.48, 128.16, 126.77, 121.94, 85.46, 84.50. MS(MALDI) *m*/*z*: 620.1 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 416 (5.3), 513 (4.11), 549 (3.79), 5.85 (3.71), 639 (3.43). HRMS(MALDI) calcd for $C_{36}H_{22}N_4F_4{}^{35}Cl$: 621.1464; found: 621.1435.

Zinc(II) 5-Ethynyl-15-perfluorohexyl-10,20-diphenylporphyrin (Zn11c). Similarly, the title compound was obtained quantitatively by the desilylation of **Zn7ca** (50 mg, 0.053 mmol) with (*n*-Bu)$_4$NF (1 M, 1 mL, in THF).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.73 (m, 2H), 9.56 (m, 2H), 9.02 (d, J = 4.8 Hz, 2H), 8.94 (d, J = 4.9 Hz, 2H), 8.18−8.14 (m, 4H), 7.83−7.78 (m, 6H), 4.16 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −77.16 (m, 2F), −80.86 (t, J = 10 Hz, 3F), −115.06 (m, 2F), −121.27 (m, 2F), −122.60 (m, 2F), −126.17 (m, 2F). MS(MALDI) *m*/*z*: 866.1 (M^+). UV−vis λ_{max} (log ϵ, THF): 426 (5.55), 564 (4.21), 601 (4.33). HRMS(MALDI) calcd for $C_{40}H_{19}N_4{}^{65}ZnF_{13}$: 866.0688; found: 866.0699.

Zinc(II) 2-Ethynyl-10-(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (Zn12b). Similarly, the title compound was obtained quantitatively by desilylation of **Zn10ba** (50 mg, 0.066 mmol) with (*n*-Bu)$_4$NF (1 M, 1 mL, in THF), followed by demetalation with 36% HCl(aq) to obtain the corresponding free base **12b** quantitatively.

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.13 (s, 1H), 9.64 (m, 2H), 9.12 (d, J = 4.5 Hz, 1H), 9.07−9.04 (d+s, overlapped, 3H), 8.85 (d, J = 4.3 Hz, 1H), 8.18−8.12 (m, 4H), 7.84−7.76 (m, 6H), 4.01 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.14 (s, 2F), −74.58 (s, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.77, 150.52, 149.79, 149.17, 148.97, 148.94, 148.50, 142.11, 141.93, 135.28, 134.33, 133.96, 133.09, 132.54, 132.28, 132.25, 132.13, 132.03, 131.99, 131.88, 128.00, 127.89, 126.77, 126.73, 125.06, 122.06, 121.65, 119.96, 106.60, 85.87, 78.85. MS(MALDI) *m*/*z*: 682.1 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 417 (5.56), 547 (4.18), 581 (4.14). HRMS(MALDI) calcd for $C_{36}H_{19}N_4F_4{}^{35}Cl^{65}Zn$: 682.0520; found: 682.0546.

2-Ethynyl-10-(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (12b). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.50 (s, 1H), 9.62 (m, 1H), 9.46 (m, 1H), 9.41 (d, J = 4.8 Hz, 1H), 9.06 (d, J = 5.6H, 1H), 8.97−8.95 (s + d, overlapped, 2H), 8.89 (d, J = 5.3 Hz, 1H), 8.21−8.17 (m, 4H), 7.84−7.76 (m, 6H), 4.06 (s, 1H), −2.85 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −63.14 (s, 2F), −74.58 (s, 2F). MS(MALDI) *m*/*z*: 620.1 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 416 (5.3), 513 (4.11), 549 (3.79), 5.85 (3.71), 639 (3.43). HRMS(MALDI) calcd for $C_{36}H_{22}N_4F_4{}^{35}Cl$: 621.1464; found: 621.1435.

Zinc(II) 2-Ethynyl-10-perfluorohexyl-5,15-diphenylporphyrin (Zn12c). Similarly, the title compound was obtained quantitatively by desilylation of **Zn10ca** (50 mg, 0.053 mmol) with Bu_4NF (1 M, 1 mL, in THF).

^{1}H NMR ($CDCl_3$, 300 MHz) δ: 10.44 (s, 1H), 9.56 (m, 2H), 9.35 (d, J = 4.6 Hz, 1H), 9.09 (s, 1H), 9.04 (d, J = 5.4 Hz, 1H), 9.03 (d, J = 5.2 Hz, 1H), 8.93 (d, J = 4.5 Hz, 1H), 8.18 (m, 4H), 7.82−7.76 (m, 6H), 4.05 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ: −76.14 (m, 2F), −80.61 (m, 3F), −114.64 (m, 2F), −120.92 (m, 2F), −122.25 (m, 2F), −125.80 (m, 2F). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.89, 150.60, 149.79, 149.10, 148.94, 148.54, 142.34, 142.13, 135.31, 134.39, 134.36, 134.32, 133.97, 133.19, 132.54, 127.91, 127.81, 126.69, 126.66, 125.00, 122.06, 121.65, 106.93, 85.70, 79.07. MS(MALDI) *m*/*z*: 866.1 (M^+). UV−vis λ_{max} (log ϵ, CH_2Cl_2): 416 (5.18), 546 (3.82), 579 (3.81). HRMS(MALDI) calcd for $C_{40}H_{19}N_4F_{13}{}^{65}Zn$: 866.0688; found: 866.0692. Anal. calcd for $C_{40}H_{19}N_4F_{13}Zn$: C, 55.35; H, 2.21; N, 6.45; found: C, 55.14; H, 2.76; N, 5.67.

Synthesis of Dimer Zn13b. A mixture of **Zn11b** (30 mg, 0.04 mmol), $Pd(PPh_3)_2Cl_2$ (2 mg), CuI (1 mg), and triethylamine (2 mL) was stirred in THF (20 mL) at room temperature under air for 1 h. The resulting green solution was passed through a short pad column of silica gel and then evaporated to dryness, and the residue was recrystallized from CH_2Cl_2/pentane to afford **Zn13b** (28 mg, 93%).

^{1}H NMR (THF-d_8, 300 MHz) δ: 9.85 (d, J = 4.5 Hz, 4H), 9.43 (m, 4H), 8.85 (d, J = 4.3 Hz, 4H), 8.79 (d, J = 5.1 Hz, 4H), 8.13−8.10 (m, 8H), 7.71−7.67 (m, 12H). ^{19}F NMR (THF-d_8, 282 MHz) δ: −64.26 (s, 2F), −75.78 (s, 2F). ^{13}C NMR (THF-d_8, 75 MHz) δ: 150.47, 148.77, 148.06, 141.00, 132.43, 131.29, 130.69, 129.76, 129.63, 129.06, 126.28, 126.12, 125.81, 124.57, 121.16, 99.01, 85.88, 80.47. MS(MALDI) *m*/*z*: 1362.2 (M^+). UV−vis λ_{max} (log ϵ, THF): 422 (4.96), 448 (5.11), 481 (4.86), 567 (4.03), 617 (4.09), 643 (4.33), 694 (4.37). HRMS(MALDI) calcd for: $C_{72}H_{36}N_8F_8{}^{35}Cl_2{}^{65}Zn_2$: 1362.0890; found: 1362.0910.

Synthesis of Dimer Zn13c. A mixture of **Zn11c** (30 mg, 0.035 mmol), $Pd(PPh_3)_2Cl_2$ (2 mg), CuI (1 mg), and triethylamine (2 mL) was stirred in THF (20 mL) at room temperature under air for 1 h.

The resulting green solution was passed through a short pad column of silica gel and then evaporated to dryness, and the residue was recrystallized from CH_2Cl_2/pentane to afford **Zn13c** (29 mg, 97%).

^{1}H NMR (THF-d_8, 300 MHz) δ: 10.00 (d, J = 4.5 Hz, 2H), 9.63 (m, 2H), 9.00 (d, J = 4.6 Hz, 2H), 8.96 (d, J = 4.5 Hz, 2H), 8.25 (d, J = 6.3 Hz, 4H), 7.86−7.81 (m, 6H). ^{19}F NMR (THF-d_8, 282 MHz) δ: −77.40 (m, 2F), −81.88 (t, J = 10.0 Hz, 3F), −115.32 (m, 2F), −121.63 (m, 2F), −123.06 (m, 2F), −126.71 (m, 2F). ^{13}C NMR (THF-d_8, 75 MHz) δ: 150.46, 148.83, 148.04, 140.91, 132.44, 131.51, 130.75, 129.16, 125.86, 124.60, 121.34, 85.82, 80.51. MS(MALDI) *m*/*z*: 1730.2 (M^+). UV−vis λ_{max} (log ϵ, THF): 424 (4.98), 447 (5.0), 481 (4.7), 566 (4.14), 614 (4.17), 642 (4.3), 694 (4.25). HRMS(MALDI) calcd for $C_{80}H_{36}N_8{}^{65}Zn_2F_{26}$: 1730.1225; found: 1730.1198.

Synthesis of Dimer Zn14b. A mixture of **Zn12b** (20 mg, 0.027 mmol), $Pd(PPh_3)_2Cl_2$ (2 mg), CuI (1 mg), and triethylamine (2 mL) was stirred in THF (20 mL) at room temperature under air for 1 h. The resulting light-brown solution was passed through a short pad column of silica gel and then evaporated to dryness, and the residue was recrystallized from CH_2Cl_2/pentane to afford **Zn14b** (19 mg, 95%).

^{1}H NMR (THF-d_8, 300 MHz) δ: 10.57 (s, 2H), 9.47 (d, J = 4.4 Hz, 6H), 9.11 (s, 2H), 8.89 (d, J = 5.4 Hz, 2H), 8.86 (d, J = 5.1 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H), 8.15−8.08 (m, 8H), 7.75−7.67 (m, 12H). ^{19}F NMR (THF-d_8, 282 MHz) δ: −66.67 (s, 4F), −76.85 (s, 4F). ^{13}C NMR (THF-d_8/$CDCl_3$, 75 MHz) δ: 150.42, 148.97, 148.15, 147.58, 147.17, 147.04, 146.91, 140.87, 140.70, 133.59, 133.57, 132.49, 132.46, 131.69, 131.41, 130.44, 129.82, 129.78, 125.90, 125.72, 124.67, 124.58, 122.33, 120.12, 119.48, 104.95, 80.71, 78.05. MS(MALDI) *m*/*z*: 1362.1 (M^+). UV−vis λ_{max} (log ϵ, THF): 428 (5.31), 450 (5.06), 480 (4.79), 564 (4.37), 607 (4.63). HRMS(MALDI) calcd for $C_{72}H_{36}N_8F_8{}^{35}Cl_2{}^{65}Zn_2$: 1362.0890; found: 1362.0910.

Synthesis of Dimer Zn14c. A mixture of **Zn12c** (20 mg, 0.023 mmol), $Pd(PPh_3)_2Cl_2$ (2 mg), CuI (1 mg), and triethylamine (2 mL) was stirred in THF (20 mL) at room temperature under air for 1 h. The resulting light-brown solution was passed through a short pad column of silica gel and then evaporated to dryness, and the residue was recrystallized from CH_2Cl_2/pentane to afford **Zn14c** (19 mg, 95%).

^{1}H NMR (THF-d_8, 300 MHz) δ: 10.58 (s, 2H), 9.48 (d, J = 4.2 Hz, 2H), 9.41 (s, 4H), 9.12 (s, 2H), 8.91 (d, J = 5.1 Hz, 2H), 8.88 (d, J = 4.7 Hz, 2H), 8.80 (d, J = 4.5 Hz, 2H), 8.16−8.09 (m, 8H), 7.75−7.67 (m, 12H). ^{19}F NMR (THF-d_8, 282 MHz) δ: −76.41 (m, 2F), −81.59 (t, J = 9.9 Hz, 3F), −115.06 (m, 2F), −121.41 (m, 2F), −122.84 (m, 2F), −126.52 (m, 2F). ^{13}C NMR (THF-d_8, 75 MHz) δ: 152.51, 150.87, 150.05, 149.65, 149.02, 148.87, 148.80, 142.78, 142.59, 135.40, 134.38, 133.48, 132.22, 131.44, 131.23, 127.93, 127.80, 127.61, 126.53, 126.43, 124.09, 122.32, 121.63, 107.01, 82.31, 79.79. MS(MALDI) *m*/*z*: 1730.1 (M^+). UV−vis λ_{max} (relative intensity, THF): 425 (5.8), 447 (3.1), 475 (1.4), 559 (0.6), 600 (1). HRMS(MALDI) calcd for $C_{80}H_{36}N_8F_{26}{}^{65}Zn_2$: 1730.1225; found: 1730.1224.

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Supporting Information Available: Characterization data (^{1}H, ^{19}F, and ^{13}C NMR spectra) for all new porphyrins. This material is available free of charge via the Internet at http://pubs.acs.org.

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