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Fluoroalkylation of Porphyrins: Synthesis and Reactions of β-Fluoroalkyltetraarylporphyrins

Li-Mei Jin,[†] Zhuo Zeng,[†] Can-Cheng Guo,*[,†] and Qing-Yun Chen*[,†,‡]

College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China, and Laboratary of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, 200032, China

chenqy@pub.sioc.ac.cn

Received December 5, 2002

Treatment of 5,10,15,20-tetraarylporphyrins (**1**) with perfluoroalkyl iodides (**2**) in the presence of $Na_2S_2O_4/NaHCO_3$ in $DMSO-CH_2Cl_2$ at 30−40 °C for several hours gives the corresponding 2-perfluoroalkylporphyrins (**3**). Nucleophilic attack on **3** with dimethyl malonate, diethyl malonate, malonitrile, or cyano acetate (Nu) anion results in the formation of (*E*)-3-Nu-2-perfuoroalkyl-(methylenyl)chlorins. Electrophilic substitution on **3** with NBS or NO_2 affords regioselectively the corresponding 12(or 13)-bromo- and 12,13-dibromo- or nitroporphyrins.

Introduction

Porphyrins demonstrate great application in various scientific fields such as biomimetic models for photosynthesis, catalysis, superamolecular chemistry, and medical applications, such as photodynamic therapy.[1] Introduction of fluorine or a fluoroalkyl group at the periphery of porphyrins has deep effect on the properties of the ligands.[2] For example, 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.[3] The synthesis of fluorinated analogues of natural porphyrins potentially useful for the diagnosis and therapy of cancer has been also achieved.[4] However, development of new methodologies to functionalize porphyrins and their derivatives at the β- and meso-position is still an active and exciting area due to providing a variety new compounds that could otherwise only be obtained by total synthesis.[5] Because the peripheral β,β-double bonds of porphyrin macrocycle are partially isolated from the macrocylic conjugation pathway, i.e., similar to normal alkenes, the chemistry of these double bonds has been greatly developed, such as hydrogenation,[6] oxidation with OsO_4,[7] Diels−Alder reaction,[8] 1,3-dipolar cycloadditions,[9] nitration,[10] and bromination.[11] 2-Nitro-5,10,15,20-tetraphenylporphyrin, as a model compound, undergoes Michael additions with a wide range of nucleophiles (hydroxide, alkoxide,[12] active methylene compounds[13]), affording 2-substituted, 2-nitro-3-substituted porphyrin and trans-functionalized chlorin. On the other hand, the nitro group can direct electrophilic substitutions to the localized double bond on the antipodal pyrrole ring, e.g., bromination of H_2(2-NO_2TPP) with NBS gave regioselectively 12,13-Br_2TPP[11b] (Figure 1).

[†] Hunan University.

[‡] Chinese Acedemy of Sciences.

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10.1021/jo0207269 CCC: $25.00
Published on Web 04/12/2003

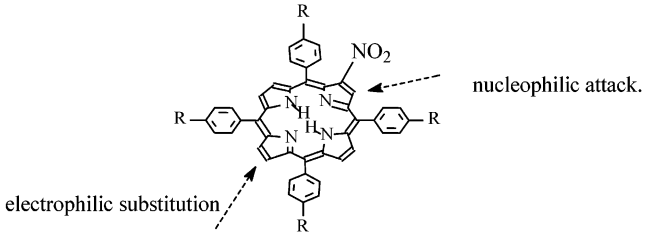
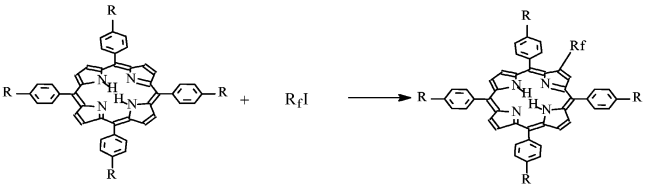


FIGURE 1. Reactivities of NH(22)-NH(24)-2-NO_2TPP.

SCHEME 1. Fluoroalkylation of 1



R=H (a) =CF_3 (b) =OCH_3 (c) =Cl (d)

R_f = n-C_4F_9 (a); = n-C_4F_8Cl (b); = n-C_6F_{13} (c); =$(CF_2)_2O(CF_2)_2SO_2F$ (d); =$(CF_2)_6O(CF_2)_2SO_2F$ (e);

In connection with our continuing interest in fluoroalkylation of organic compounds,[14] we envisioned that the perfluoroalkyl group might be introduced onto peripheral β,β-double bonds of the porphyrin macrocycle with perfluoroalkyl iodides and chemical transformations would take place subsequently. Herein we present the results.

Results and Discussion

Synthesis of β-Fluoroalkyltetraarylporphyrins. Although there might be several methods for fluoroalkylation of β,β-double of porphyrins, it was found that the sulfinatodehalogenation method is most suitable to introduce the perfluoroalkyl group onto a β,β-double carbon−carbon bond; i.e., treatment of tetraphenylporphyrin (H_2TPP, **1a**), tetra(*p*-trifluoromethylphenyl)porphyrin (H_2T(*p*-CF_3)PP, **1b**), tetra(*p*-methoxyphenyl)porphyrin (H_2T(*p*-CH_3O)PP, **1c**), and tetra(*p*-chlorophenyl)porphyrin (H_2T(*p*-CI)PP, **1d**) with perfluoroalkyl iodides (R_fI, **2**) in the presence of $Na_2S_2O_4$ and $NaHCO_3$ in a mixture solvent of DMSO/CH_2Cl_2 at room temperature for several hours gave the corresponding β-perfluoroalkyl porphyrins (**3**) in 20−35% yields (Scheme 1).

The amounts of reactants R_fI and $Na_2S_2O_4$ and solvent used as well as reaction temperature were shown to have an influence on the yield of **3**. For example, because porphyrins are poorly soluble in DMSO at room temperature, a cosolvent, CH_2Cl_2 was necessary, the optimal ratio of DMSO−CH_2Cl_2 being 1:1 by volume. Perfluoroalkyl iodides should be added in large excess, usually in 30−50 equiv, otherwise the reaction proceeded very slowly, e.g., none of **3** was detected after 4 days if 1 equiv of R_fI relative to **1** was employed. Reaction temperature was also found to influence the yield of the products; for example, below 10 °C, the reaction did not take place, and when above 80 °C, side products formed that were not identified and that render the separation of the desired compounds more difficult to achieve. Notably, at 30−40 °C, the most suitable reaction temperature, only the carbon−iodine bond in chloroperfluorobutyl iodides **2b** was cleaved while the carbon−chlorine bond remained intact, which is in consonance with the previous observation.[15d,e] The results are listed in Table 1.

TABLE 1. Reaction of Porphyrin (1) with Perfluoroalkyl Iodide (2) in the Presence of $Na_2S_2O_4$/$NaHCO_3$ in DMSO−CH_2Cl_2

porphyrin (**1**)	R_fI (**2**)	*T*/°C	*t*/h	**3**	yield/%[a]
1a	**2a**	35	18	**3aa**	35
	2b	35	18	**3ab**	35
	2d	35	18	**3ad**	30
	2e	35	18	**3ae**	35
1b	**2a**	30	8	**3ba**	30
	2d	30	8	**3bd**	30
1c	**2c**	30	6	**3ca**	20
1d	**2a**	30	10	**3da**	25
	2b	30	10	**3db**	20
	2c	30	10	**3dc**	20
	2d	30	10	**3dd**	20

[a] Based on the consumed H_2TPP.

TABLE 2. Inhibition Experiments[a]

	% conversion of H_2TPP[b]		
t/h	A	B	C
10	25	0	0
20	70	0	0
30	100	0	0

[a] A: The samples of H_2TPP (8 mg, 13 mol), C_4F_9I (225 mg, 0.65 mmol), $Na_2S_2O_4$ (113 mg, 0.65 mmol), $NaHCO_3$ (55 mg, 0.65 mmol) dissolved in a mixture solvents of CH_2Cl_2 (5 mL), and DMSO (5 mL), stirred at room temperature. B: A plus HQ (20 mol %). C: A plus *p*-DNB (20 mol %). [b] Determined by ^{19}F NMR and TLC.

Interestingly, the β-fluoroalkylporphyrins (**3**) were obtained rather than 2,3-dihydroporphyrin (chlorin), although a trace of the latter was also detected by the appearance of a long wavelength peak at λ_{max} = 650 nm of UV−vis absorption. The structure of the product **3** was unambiguously assigned by ^{1}H, ^{19}F, ^{13}C NMR and MS as well as well elemental analysis. The pronounced red-shift of the Soret band, 5−7 nm per β-substituent, and Q-bands relative to the parent compounds strongly supported this conclusion.

To understand the reaction mechanism, some inhibition experiments were carried out. Addition of electron-transfer scavenger, i.e., *p*-dinitrobenzene (*p*-DNB) (20 mol %), or free radical inhibitor, i.e., hydroquinone (HQ) (20 mol %), to the reaction mixture of **1a** completely suppressed the reaction at the same reaction temperature and time (see Table 2). On the basis of the experiments, perfluoroalkyl radical may be involved. The most likely explanation of generation of R_f• is that R_fI accepts one electron from the radical anion of sulfur dioxide, produced by decomposition of $Na_2S_2O_4$, then dissociated to give R_f• and I^-.[15] The R_f• added to β,β-double bond of porphyrins, like to normal alkenes to form intermediate **A**. The intermediate **A** did not abstract iodine from R_fI, as we

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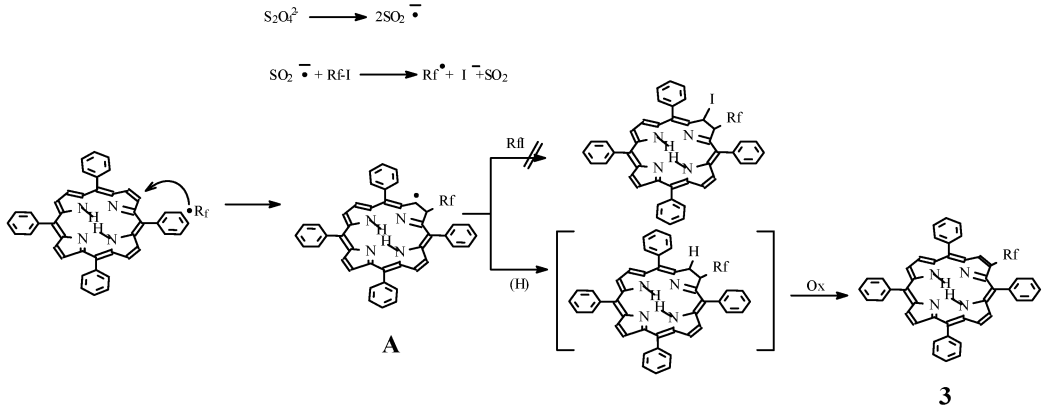
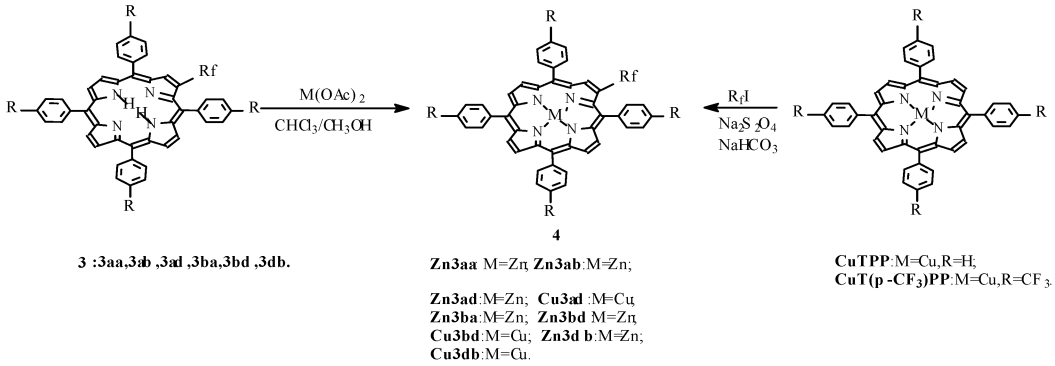


FIGURE 2. The possible mechanism for the formation of **3**.

SCHEME 2. Metalation of 3



3 :**3aa**,**3ab** ,**3ad** ,**3ba**,**3bd** ,**3db**.

Zn3aa: M=Zn; **Zn3ab**:M=Zn;
Zn3ad:M=Zn; **Cu3ad** :M=Cu;
Zn3ba:M=Zn; **Zn3bd** M=Zn;
Cu3bd:M=Cu; **Zn3d b**:M=Zn;
Cu3db:M=Cu.

CuTPP:M=Cu,R=H;
CuT(p-CF_3)PP:M=Cu,R=CF_3.

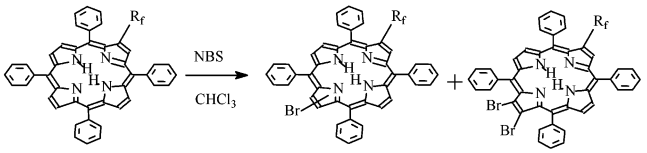
previously reported,[15d,e] but easily picked up hydrogen from DMSO to afford β- perfluoroalkylporphyrin through the quick oxidation of unstable 2,3-dihydroporphyrin (chlorin). The phenomenon is similar to the bromination of 5,10,15,20-tetraphenylporphyrins resulting in the formation of 7,8-dibromoporphyrins after the oxidation of the corresponding chlorin by bromine.[11b] Both weak oxidants, R_fI and DMSO,[16] might play a remarkable role in our case for the formation of **3**. (Figure 2)

The zinc and copper 2-fluoroalkyl-5,10,15,20-tetraarylporphyrin complexes can be readily prepared nearly quantitatively from the reaction of the corresponding porphyrins with zinc or copper acetate in CH_2Cl_2–CH_3OH at room temperature for 30 min (Scheme 2).

The same 2-perfluoroalkylmetalloporphyrins can also be synthesized via fluoroalkylation of the corresponding metalloporphyrins; e.g., CuTPP or CuT(*p*-CF_3)PP reacted with R_fI in the presence of $Na_2S_2O_4$/$NaHCO_3$ in DMSO−CH_2Cl_2, producing the corresponding 2-fluoroalkylmetalloporphyrins.

Reactions of 2-Perfluoroalkyltetraarylporphyrins. To further functionalize the β-fluoroalkyltetraarylporphyrins, electrophilic substitutions on the antipodal β,β-double bond were first investigated, i.e., bromination of **3ad**.[11b] Treatment of **3ad** with 2.6 equiv of *N*-bromosuccimimide (NBS) in boiling ethanol-free chloroform afforded a mixture of the corresponding 2-perfluoroalkyl-12,13-dibromo (45%) and 12(or 13)-monobromotetraarylporphyrins (48%). These structures

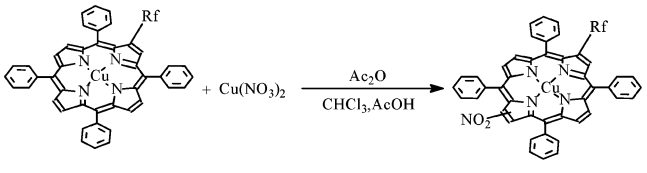
SCHEME 3. Bromination of 3ad



R_f= $CF_2CF_2OCF_2CF_2SO_2F$

(3ad) **(5ad1)** **(5ad2)**

SCHEME 4. Nitration of Cu3ad



(Cu3ad) Rf=$CF_2CF_2OCF_2CF_2SO_2F$ **6**

were readily assigned by ^1H,^{19}F NMR and MS, as well as UV−vis spectra. However, the position of bromine in the monobromide was not yet determined. Similarly, one nitro group could be introduced onto the antipodal pyrrolenic position by the reaction of Cu(2-R_f)TPP with $Cu(NO_3)_2$.[17] Likewise, the position of the nitro group was not assigned. On the other hand, β-fluoroalkyltetraarylporphyrins were also subjected to nucleophilic attack. Thus, when **3ab** reacted with "active" methylene compounds (NuH), such as dimethyl malonate, diethyl mal-

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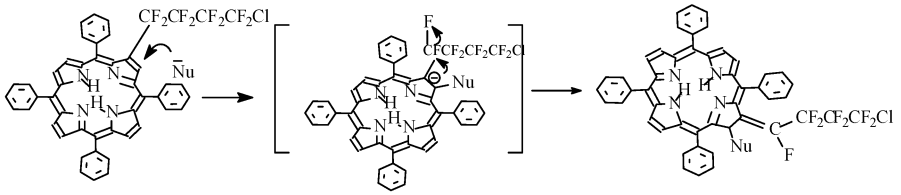

3ab **7**

Nu= $CH(CO_2Me)_2$ **(7a)** ;$CH(CO_2Et)_2$ **(7b)**; $CH(CN)CO_2Me$ **(7c)** ;$CH(CN)_2$ **(7d)**.

FIGURE 3. The possible mechanism for the formation of **7**.

onate, malonitrile, and methyl cyanoacetate in the presence of K_2CO_3 at 70 °C in DMSO for 7−8 h, 3-Nu-2-perfluoroalkylmethylenylchlorins **7** were obtained with only *E*-configuration (Figure 3).

The structure of **7** was fully established by IR; ^{1}H, ^{19}F, ^{13}C NMR; ^{13}C-DEPT; MS; and UV−vis as well as elementary analysis.

The formation of **7** is easily understood by the following mechanism. Nucleophilic addition of "active" methylene carbanion to the 2-fluoroalkyl pyrrolenic double bond results in the generation of anion at the neighboring carbon-bearing perfluoroalkyl group, which affords the product after elimination of fluoride ion. The presence of *p*-dinitrobenzene (20 mol %) or hydroquinone (20 mol %) in the reaction mixture of **3** and nucleophile (Nu^-) at the same temperature and time did not decrease the conversion of **3ab** and yield of **7**, supporting the above ionic rather than free radical mechanism.

Finally, it is worth mentioning the tautomerism of 2-substituted 5,10,15,20-tetraarylporphyrins. Crossley and co-workers showed that in the tautomeric equilibrium when R = NO_2, CHO, Cl, Br, OMe, CN, NHCOMe, SPh, OCOPh, or OH, the dominant tautomer is that R lies on the isolated double bond, while for R = CH=CH_2, CH_2OH, NH_2, Me, $CH(Me)_2$, or $(CH_2)_3Me$, the major tautomer is one where R lies on the aromatic delocalization pathway.[18] On the basis of our above results, in the case of free base **3**, the tautomer of 2-fluoroalkyl-5,10,-15,20-tetraphenyl 22-H,24-H porphyrin, in which there is an isolated fluoroalkylethene system, is heavily more favored in solution at tautomeric equilibrium.

In conclusion, we have developed for the first time a practical method for synthesizing β-fluoroalkyltetraarylporphyrins from simple, available porphyrins and perfluoroalkyl iodides by a sulfinatodehalogenation method. Some nucleophilic addition and electrophilic substitution reactions of the β-fluoroalkylporphyrins show that the β,β-bond bearing perfluoroalkyl group can behave as a fluoroalkylethene system without disrupting the aromaticity of the macrocycle of the porphyrin.

Experimental Section

^{1}H NMR spectra were recorded with trimethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were recorded with $CFCl_3$ as an external standard (negative for upfield). The solvent for NMR measurement was $CDCl_3$ or CD_3COCD_3.

Porphyrins of H_2TPP, $H_2T(p\text{-}CF_3)PP$, $H_2T(p\text{-}CH_3O)PP$, $H_2T(p\text{-}Cl)PP$, and the corresponding metal porphyrins were prepared by literature methods.[19]

Typical Procedure for Perfluoroalkylation of the Porphyrins. The sample of porphyrin (0.2 mmol) was dissolved in the mixture of DMSO:CH_2Cl_2 1:1 vol (160 mL), then a large excess of R_fI (10 mmol), $NaHCO_3$ (10 mmol), and $Na_2S_2O_4$ (10 mmol) was added in order. The mixture was stirred for 8−20 h at 30 °C. The course of the reaction was monitored by TLC. When most of the starting materials was consumed, the mixture was washed with water several times. The organic layer was dried over anhydrous Na_2SO_4 and rotary evaporated to dryness. The crude products were purified by dry column chromatography, using hexane:dichloromethane (1:1 vol) as eluent. The red-purple band and dark-purple band were dug out and respectively washed with CH_2Cl_2. The red-purple band was unconsumed material. The dark-purple band was further purified by flash chromatography [300−400 mesh silica gel, petroleum ether:dichloromethane (3:1 vol)] to yield a light purple solid that was recrystallized from CH_2Cl_2–methanol.

2-(Nanofluorobutyl)-5,10,15,20-tetraphenylporphyrin (3aa). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.59 (br s, 2H), 7.18−8.25 (m, 20H), 8.67−8.92 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 120.28, 120.34, 121.5, 122.1, 125.9, 126.78, 126.81, 126.93, 127.9, 128.15, 128.26, 128.5, 128.95, 130.1, 131.2, 133.9, 134.2, 134.7, 134.9, 135.04, 139.8, 141.3, 141.6, 141.9, 147.1, 154.2. ^{19}F NMR (282 MHz, CDCl3) δ (ppm): −80.98 (s, 2F), −96.88 (s, 2F), −118.69 (s, 2F), −125.23 (t, J = 15 Hz, 3F). MS (ESI) m/z: 833.1 (M^+ + 1). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 657 (1), 600 (0.6), 557 (0.7), 522 (2.1), 422 (46.2). Anal. Calcd for $C_{48}H_{29}N_4F_9 \cdot 1.5H_2O$: C, 67.05; H, 3.73; N, 6.52; F, 19.91. Found: C, 67.26; H, 3.66; N, 6.40; F, 19.62.

2-(4-Chlorooctafluorobutyl)-5,10,15,20-tetraphenylporphyrin (3ab). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.6 (brs, 2H), 7.5−8.5 (m, 20H), 8.5−9.0 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −67.89 (t, J = 11.2 Hz, 2F), −97.0 (m, 2F), −117.1 (m, 2F), −119.2 (m, 2F). MS (EI, relative intensity) m/z: 848 (M^+, 70). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 657 (1), 601 (0.6), 556 (0.8), 522 (2.1), 422 (45.2). Anal. Calcd for $C_{48}H_{29}F_8ClN_4$: C, 67.89; H, 3.44; N, 6.60; F, 17.90. Found: C, 67.45, H, 3.59; N, 5.5; F, 17.47.

2-(3-Oxa-ω-fluorosulfonylperfluoropentanyl)-5,10,15,-20-tetraphenylporphyrin (3ad). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.63 (br s, 2H), 7.62−7.81 (m, 12H), 8.13−8.21 (m, 8H), 8.66−9.02 (m, 7H). ^{19}F NMR(282 MHz, $CDCl_3$) δ (ppm): 45.87 (m, 1F), −81.92 (m, 2F), −83.2 (m, 2F), −97.08 (m, 2F), −111.98 (m, 2F). MS (EI, relative intensity) m/z: 913 (M^+ + 1, 100). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 657 (1), 600 (0.6), 557 (0.9), 521 (2.2), 421 (49.1). Anal. Calcd for $C_{48}H_{29}N_4F_9SO_3 \cdot 0.5H_2O$: C, 62.54; H, 3.26; N, 6.08; F, 18.57; S, 3.47. Found: C, 62.13; H, 3.11; N, 5.88; F, 18.97; S, 3.70.

2-(7-Oxa-ω-fluorosulfonylperfluorononanoyl)-5,10,15,20-tetraphenylporphyrin (3ae). ^{1}H NMR (300 MHz, $CDCl_3$) δ

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(ppm): −2.58 (br s, 2H), 7.63−8.24 (m, 20H), 8.71−9.04 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): 46.09 (s, 1F), −81.79 (s, 2F), −82.68 (t, 2F, J = 7.8 Hz), −97.06 (t, 2F, J = 6.75 Hz), −112.08 (s, 2F), −117.83 (s, 2F),-121.22 (s, 2F), −122.23 (s, 2F), −125.17 (s, 2F). MS (EI, relative intensity) m/z: 1113 (M^+ + 1, 95.11). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 658 (1), 600 (0.9), 521 (2.3), 422 (50.4). Anal. Calcd for $C_{52}H_{29}N_4F_{17}SO_3$: C, 56.12; H, 2.63; N, 5.03; F, 29.02. Found: C, 55.96; H, 2.65; N, 5.01; F, 29.00.

2-Perfluorobutyl-5,10,15,20-tetrakis(4-trifluoromethylphenyl)porphyrin (3ba). ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm): −2.67 (s, 2H), 7.93−8.34 (m, 16H), 8.64−9.02 (m, 7H). ^{19}F NMR(282 MHz,$CDCl_3$) δ (ppm): −62.22 (m, 12F), −81.06 (s, 3F), −96.81 (2F), −118.66 (2F), 125.42 (t, 2F). MS (ESI) m/z: 1105.2 (MH^+). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 655 (1), 596 (0.8), 555 (0.8), 520 (2.7), 421 (55.2). Anal. Calcd for $C_{52}H_{25}N_4F_{21}\cdot 0.5H_2O$: C, 56.06; H, 2.25; N, 5.03; F, 35.84. Found: C, 55.99; H, 2.57; N, 4.93; F, 35.74.

2-(3-Oxa-ω-fluorosulfonylperfluoropentanyl)-5,10,15,-20-tetrakis(4-trifluomethylphenyl)porphyrin (3bd). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.68 (s, 2H), 7.94−8.34 (m, 16H), 8.64−8.98 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): 45.72 (s, 1F), −62.29 (m, 12F), −82.06 (2F), −82.88 (2F), −96.65 (2F), −112.2 (2F). MS (EI, relative intensity) m/z: 1185 (M^+ + 1, 93.06). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 655 (1), 599 (0.6), 521 (2.4), 421 (51.2). Anal. Calcd for $C_{52}H_{25}N_4F_{21}SO_3\cdot H_2O$: C, 51.91; H, 2.24; N, 4.66; F, 33.19; S, 2.66. Found: C, 51.47; H, 2.19; N, 4.66; F, 33.13; S, 2.72.

2-Perfluorohexyl-5,10,15,20-tetrakis(4-methoxylphenyl)-porphyrin (3cb). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.56 (br s, 2H), 4.01−4.13 (m, 12H), 7.18−8.16 (m, 16H), 8.7−8.88 (m, 7H). ^{1}F NMR (282 MHz, $CDCl_3$) δ (ppm): −80.81 (d, 3F), −96.74 (d, 2F), −118 (s, 2F), −121.25 (s, 2F), −122.82 (s, 2F), −126.06 (s, 2F). MS (EI, relative intensity) m/z:1053 (M^+ + 1, 50.57). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 667 (1), 563 (0.9), 526 (1.6), 427 (39). Anal. Calcd for $C_{54}H_{37}N_4O_4F_{13}\cdot H_2O$: C, 60.56; H, 3.64; N, 5.23. Found: C, 60.57; H, 3.64; N, 4.91.

2-Perfluorobutyl-5,10,15,20-tetrakis(4-chlorophenyl)-porphyrin (3da). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.7 (s, 2H), 7.73−7.78 (m, 8H), 8.1−8.14 (m, 8H), 8.5−9.0 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −81.01 (d, J = 6 Hz, 3F), −96.7 (d, J = 7.5 Hz, 2F), −118.78 (d, J = 4.5 Hz, 2F), −125.3 (t, J = 15 Hz, 2F). MS (EI, relative intensity) m/z: 972 (M^+ + 1, 100). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 655 (1), 599 (0.6), 522 (2.2), 423 (47.9). Anal. Calcd for $C_{48}H_{25}N_4Cl_4F_9$: C, 59.4; H, 2.6; N, 5.77; F, 17.62. Found: C, 58.87; H, 2.88; N, 5.61; F, 17.56.

2-(4-Chlorooctafluorobutyl)-5,10,15,20-tetrakis(4-chlorophenyl)porphyrin (3db). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.69 (s, 2H), 7.56−8.24 (m, 16H), 8.65−9.02 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −68.04 (2F), −96.78 (2F), −117.41 (2F), −119.44 (2F). MS (EI, relative intensity) m/z: 987 (M^+, 28.7). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 652 (1), 599 (0.7), 523 (1.9), 424 (36). Anal. Calcd for $C_{48}H_{25}N_4F_8Cl_5$: C, 58.41; H, 2.55; N, 5.68; F, 15.4. Found: C, 58.25; H, 2.60; N, 5.57; F, 15.17.

2-Perfluorohexyl-5,10,15,20-tetrakis(4-chlorophenyl)-porphyrin (3dc). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.68 (brs, 2H), 7.66−8.17 (m, 16H), 8.7−8.89 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −80.77 (t, 3F), −96.7 (t, 2F), −117.88 (s, 2F), −121.23 (s, 2F), −122.81 (s, 2F), −126.05 (s, 2F). MS (EI, relative intensity) m/z: 1072 (M + 1, 6.42). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 655 (1), 602 (0.6), 521 (2.3), 423 (47.6). Anal. Calcd for $C_{50}H_{25}N_4Cl_4F_{13}\cdot 0.5H_2O$: C, 55.5; H, 2.41; N, 5.18; F, 22.85. Found: C, 55.58; H, 2.74; N, 5.07; F, 22.33.

2-(3-Oxa-ω-fluorosulfonylperfluoropentanyl)-5,10,15,-20-tetrakis(4-chlorophenyl)porphyrin (3dd). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.72 (s, 2H), 7.64−7.78 (m, 8H), 8.04−8.13 (m, 8H), 8.67−9.00 (m, 7H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): 45.79 (s, 1F), −81.99 (2F), −82.95 (2F), −96.76 (2F), −112.16 (2F). MS (EI, relative intensity) m/z: 1050 (M^+, 52.71). UV−vis λ_{max} (relative intensity, CH_3CN): 653 (1), 597 (0.5), 554 (0.6), 520 (2.3), 419 (54). Anal. Calcd for $C_{48}H_{25}N_4F_9SO_3Cl_4$: C, 54.88; H, 2.4; N, 5.33; Cl, 13.5; F, 16.27. Found: C, 54.24; H, 2.49; N, 5.19; F, 16.23.

Typical Procedure for Insertion of Metal into the Core of the Porphyrins. The samples of porphyrin (50 mg) and M(II) acetate monohydrate (5 equiv) were placed in a round-bottomed flask, then a mixture of CH_2Cl_2 (25 mL) and methanol (3 mL) was added. The mixture was stirred at room temperature for 30 min. Silica gel (1 g) was added to the reaction mixture when TLC monitoring indicated that the starting material was consumed. The solvent was evaporated and the residue subjected to flash chromatography [silica gel, petroleum ether:dichloromethane (10:1 vol)]. The main fraction was collected and evaporated to dryness to give a purple solid which was recrystallized from CH_2Cl_2−CH_3OH (or dichloromethane−hexane).

2-(Nanofluorobutyl)-5,10,15,20-tetraphenylporphinatozinc(II) (Zn3aa). UV−vis λ_{max} (relative intensity, CH_3CN): 594 (1), 554 (1.8), 423 (35). MS (MALDI) m/z: 894.1 (M^+). HRMS (MALDI) calcd for $C_{48}H_{27}F_9N_4Zn\cdot H^+$: 895.1412. Found: 895.1462.

2-(4-Chlorooctafluorobutyl)-5,10,15,20-tetraphenylporphinatozinc(II) (Zn3ab). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.61−7.75 (m, 12H), 8.07−8.19 (m, 8H), 8.6−8.9 (m, 6H), 9.3 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −67.82 (t, J = 12.6 Hz, 2F), −96.19 (t, J = 14.4 Hz, 2F), −116.55 (2F), −119.08 (t, J = 15.3 Hz, 2F). MS (EI, relative intensity) m/z: 912 (M^+, 100). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 594 (1), 555 (1.8), 423 (41). Anal. Calcd for $C_{48}H_{27}N_4F_8ClZn$: C, 63.17; H, 2.98; N, 6.14. Found: C, 63.42; H, 3.11; N, 5.73.

2-(3-Oxa-ω-fluorosulfonylperfluoropentanyl)-5,10,15,-20-tetraphenylporphinatozinc(II) (Zn3ad). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.61−7.75 (m, 12H), 8.07−8.19 (m, 8H), 8.64−8.9 (m, 6H), 9.3 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −67.82 (t, J = 11.3 Hz, 2F), −96.19 (t, J = 11.3 Hz, 2F), −116.53 (d, J = 5.7 Hz, 2F), −119.08 (t, J = 14.1 Hz, 2F). MS (EI, relative intensity) m/z: 976 (M^+, 100), 912 (M − Zn + 1, 5.36). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 599 (1), 555 (1.5), 424 (37.8). Anal. Calcd for $C_{48}H_{27}F_9N_4O_3SZn\cdot H_2O$: C, 58.00; H, 2.92; N, 5.64. Found: C, 57.99; H, 3.00; N, 5.26.

2-(3-Oxa-ω-fluorosulfonylperfluoropentanyl)-5,10,15,-20-tetraphenylporphinatocopper(II) (Cu3ad). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): 45.95 (s, 1F), −81.79 (s, 2F), −111.89 (s, 2F). MS (EI, relative intensity) m/z: 975 (M^+ + 1, 100). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 580 (1), 545 (2.6), 419 (62.2). Anal. Calcd for $C_{48}H_{27}F_9N_4O_3SCu$: C, 59.06; H, 2.79; N, 5.74. Found:C, 59.04; H, 2.83; N, 5.53.

2-Perfluorobutyl-5,10,15,20-tetrakis(4-trifluoromethylphenyl)porphinatozinc(II) (Zn3ba). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.9−8.35 (m, 16H), 8.6−8.88 (m, 6H), 9.25 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −62 (m, 12F), −81 (d, J = 1.8 Hz, 3F), −95.9 (t, J = 11.7 Hz, 2F), −118.11 (d, J = 4.7 Hz, 2F), −125.4 (t, J = 15 Hz, 2F). UV−vis λ_{max} (relative intensity, CH_3CN): 604 (1), 563 (1.6), 426 (47). MS (EI, relative intensity) m/z: 1167 (M + 1, 100). Anal. Calcd for $C_{52}H_{23}F_{21}N_4Zn$: C, 53.47; H, 1.98; N, 4.8. Found: C, 53.56; H, 2.21; N, 4.72.

2-(3-Oxa-ω-fluorosulfonylperfluoropentanyl)-5,10,15,-20-tetrakis(4-trifluomethylphenyl)porphinatozinc(II) (Zn3bd). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.91−8.33 (m, 16H), 8.58−8.89 (m, 6H), 9.2 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): 45.78 (s, 1F), −62.15 (t, J = 36.6 Hz, 12F), −82.06 (s, 2F), −82.54 (s, 2F), −95.52 (s, 2F), −112.22 (t, J = 3.9 Hz, 2F). UV−vis λ_{max} (relative intensity, CH_3CN): 603 (1), 564 (1.7), 426 (52). MS (EI, relative intensity) m/z: 1248 (M^+, 100). Anal. Calcd for $C_{52}H_{23}ZnF_{21}N_4O_3S$: C, 50.04; H, 1.84; N, 4.49. Found: C, 50.73; H, 2.25; N, 4.39.

2-(3-Oxa-ω-fluorosulfonylperfluoropentanyl)-5,10,15,-20-tetrakis(4-trifluomethylphenyl)porphinatocopper-(II) (Cu3bd). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): 45.81 (s, 1F), −62.39 (t, J = 43.2 Hz, 12F), −82.02 (s, 2F), −112.25 (s, 2F). UV−vis λ_{max} (relative intensity, CH_3CN): 581 (1), 544

(2.4), 416 (60.2). MS (EI, relative intensity) *m/z*: 1247 (M^+ + 1, 100). Anal. Calcd for $C_{52}H_{23}CuF_{21}N_4O_3S$: C, 50.11; H, 1.86; N, 4.5. Found: C, 49.78; H, 2.16; N, 4.30.

2-(4-Chlorooctafluorobutyl)-5,10,15,20-tetrakis(4-chlorophenyl)porphinatozinc(II) (Zn3db). ^{1}H NMR (300 MHz, CD_3COCD_3) δ (ppm): 7.56−8.13 (m, 16H), 8.47−9.12 (m, 7H). ^{19}F NMR (282 MHz, CD_3COCD_3) δ (ppm): −68.73 (s, 2F), −95.07 (s, 2F), −116.84 (s, 2F), −119.62 (s, 2F). UV−vis λ_{max} (relative intensity, CH_3CN): 606 (1), 563 (1.4), 427 (35). MS (EI, relative intensity) *m/z*: 1050 (M^+, 13.6). Anal. Calcd for $C_{48}H_{23}N_4F_8Cl_5Zn\cdot 2.5H_2O$: C, 52.60; H, 2.56; N, 5.11. Found: C, 52.76; H, 2.57; N, 4.95.

2-(4-Chlorooctafluorobutyl)-5,10,15,20-tetrakis(4-chlorophenyl)porphinatocopper(II) (Cu3db). UV−vis λ_{max} (relative intensity, CH_3CN): 581 (1), 544 (2), 417 (42). MS (EI, relative intensity) *m/z*: 1048 (M^+, 30.2). Anal. Calcd for $C_{48}H_{23}Cl_5CuF_8N_4$: C, 54.98; H, 2.21; N, 5.34. Found: C, 55.00; H, 2.52; N, 5.26.

Bromination of 3ad. A mixture of **3ad** (120 mg, 0.1316 mmol) and *N*-bromosuccinimide (62 mg, 0.35 mmol) in dry $CHCl_3$ (ethanol free, 60 mL) was heated under reflux overnight. After the reaction cooled to room temperature, silica gel (2 g) was added. The mixture was rotary evaporated to dryness. The crude product was purified by flash chromatography (silica gel, 300−400 mesh, petroleum ether:dichloromethane from 3:1 to 1:1 vol). The first mainly dark-purple band was collected and evaporated to dryness to afford **5ad1** (62 mg, 48%). And the second mainly dark-purple band was collected to give **5ad2** (63 mg, 45%).

5ad1 (recrystallized from $CHCl_3$−CH_3OH)**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.7 (d, 2H), 7.6−8.3 (m, 20H), 8.5−9.0 (m, 6H). ^{19}F NMR (282HMz,$CDCl_3$) δ (ppm): 45.82 (s, 1F), −82.0 (s, 2F), −83.1 (s, 2F), −97.5 (s, 2F), −112.1(s, 2F). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 661 (1.9), 602 (1), 525 (3.7), 425 (65). MS (EI, relative intensity) *m/z*: 992 (M + 1, 87.75), 913 (M − Br + 1, 82.4). Anal. Calcd for $C_{48}H_{28}N_4SF_9O_3Br$: C, 58.12; H, 2.83; N, 5.65. Found: C, 58.71; H, 3.53; N, 5.01.

5ad2 (recrystallized from CH_3Cl−CH_3OH)**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −2.69 (br s, 1H), −2.77 (br s, 1H), 7.75−8.25 (m, 20H), 8.54− 8.84 (m, 5H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): 45.74 (s, 1F), −82.06 (s, 2F), −83.50 (t, 2F), −98.32 (s, 2F), −112.13 (s, 2F). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 679 (1), 531 (1.5), 430 (27). MS (EI, relative intensity) *m/z*: 1072 (M^+ + 2, 71.51), 992 (M − Br, 68.89), 912 (M − 2Br, 100). Anal. Calcd for $C_{48}H_{27}N_4SF_9O_3Br_2$: C, 53.85; H, 2.54; N, 5.23; Br, 14.93. Found: C, 53.25; H, 2.51; N, 5.02; Br, 15.03.

Nitration of Cu3ad. $Cu(NO_3)_2$ $3H_2O$ (45 mg) in 4.5 mL of Ac_2O was added to 80 mg of **Cu3ad** dissolved in a mixture of 75 mL of $CHCl_3$ plus 1.5 mL of acetic acid. The reaction mixture was stirred at room temperature for 2 days, until no starting material was detectable by TLC [petroleum ether: dichloromethane (3:1 vol)]. The solution was subsequently washed with water and aqueous K_2CO_3 and dried over Na_2SO_4. The organic layer was evaporated to dryness. The residue was purified by flash chromatography [silica gel, 300−400 mesh, petroleum ether:dichloromethane (3:1 vol)]. The main fraction was collected and evaporated to dryness to give a purple solid **6** (recrystallized from $CHCl_3$–methanol). UV−vis λ_{max} (relative intensity, CH_3CN): 595 (1), 554 (1.5), 427 (21.4). MS (EI, relative intensity) *m/z*: 1020 (M^+ + 1, 100). HRMS (MALDI) calcd for $C_{48}H_{27}CuF_9N_5O_5S\cdot H^+$: 1019.0878. Found: 1019.0879.

Typical Procedure of Nucleophilic Addition to 3ab. A solution of K_2CO_3 (310 mg, 2.25 mmol) and dimethyl malonate (370 mg, 3.4 mmol) in dry DMSO (10 mL) was stirred for 2 h at 70 °C under argon. Compound **3ab** (85 mg, 0.1 mmol) was added, and the solution was stirred for another 8 h. The mixture was cooled to room temperature, diluted with CH_2Cl_2 (20 mL), washed with brine (5 × 20 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude mixture was purified by flash chromatography [300−400 mesh silica gel, petroleum ether:dichloromethane (2:1 vol)]. The main fraction was collected and evaporated to dryness to afford the product **7a** in 70% yield which was recrystallized from CH_2Cl_2–hexane. Additionally, it was found that the addition of *p*-DNB (20 mol %) or HQ (20 mol %) has no effect on the yields of the products.

5,10,15,20-Tetraphenyl-[2:3]-[((methoxycarbonyl)methyl)(1-fluoro-1-(3-chlorohexfluoropropyl)methylenyl)]-porphyrin (7a). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −1.41 (s, 2H), 2.49 (s, 3H), 3.03 (s, 3H), 4.15 (d, J = 1.5 Hz, 1H), 6.16 (d, J = 1.6 Hz, 1H), 7.62−8.88 (m, 26H, β-H, Ph-H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −67.66 (t, J = 11.3 Hz, 2F, −CF_2Cl), −110.9 to −111.2 (m, 3F, =CFCF_2), −119.2 to −121.9 (m, 2F, −CF_2CF_2Cl). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 47.6, 51.8, 51.9, 54.9, 112.3, 115.4, 123.0, 124.0, 125.6, 125.8, 126.9, 127.4, 127.5, 127.8, 127.9, 128, 128.4, 132.7, 133.2, 133.3, 133.9, 136.2, 140.5, 140.9, 141.7, 152.3, 153.1, 154.0, 157.9, 166.4, 166.8. DEPT (θ = 90°): 47.7, 55.0, 125.8, 126.0, 127.1, 127.6, 127.7, 128.0, 128.1, 128.2, 128.6, 128.7, 132.9, 133.4, 133.5, 134.1, 134.5, 136.5. UV−vis λ_{max} (relative intensity, CH_2Cl_2): 660 (3), 606 (1), 558 (1.8), 527 (2), 422 (30). MS (MALDI) *m/z*: 961.2 (MH^+). IR (KBr): 3344 (NH), 176 8 (−CO_2−), 1727 (−CO_2−), 1186 (CF). Anal. Calcd for $C_{53}H_{36}ClF_7N_4O_4$: C,66.22; H,3.77; N, 5.83; F, 13.83. Found: C, 66.16; H, 3.50; N, 5.59; F, 13.40.

5,10,15,20-Tetraphenyl-[2:3]-[((ethoxycarbonyl)methyl)-(1-fluoro-1-(3-chlorohexfluorpropyl)methylenyl)]porphyrin (7b). Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −1.36 (s, 2H), 0.29 (t, J = 7 Hz, 3H), 0.41 (t, J = 7 Hz, 3H), 3.1 (m, 4H), 4.21 (m, 1H), 6.22 (d, J = 1.8 Hz, 1H), 7.59−8.88 (m, 26H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −67.6 (m, 2F, −CF_2Cl), −110.9 to −111.1 (m, 2F, =CFCF_2−), −111.9 to −112.1 (m, 1F, =CFCF_2−), −119.4 to −121.9 (m, 2F, −CF_2-CF_2Cl). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 661 (1.8), 606 (1), 557 (1.5), 527 (1.7), 423 (15). MS (EI, relative intensity) *m/z*: 989 (M + 1, 60.82). Anal. Calcd for $C_{55}H_{40}F_7N_4O_4Cl$: C, 66.77; H, 4.08; N, 5.66. Found: C, 66.24; H, 4.05; N, 5.24.

5,10,15,20-Tetraphenyl-2-[(cyano)(ethoxycarbonyl)-methyl]-3-[1-fluoro-1-(3-chlorohexfluoropropyl)methylenyl]porphyrin (7c). Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −1.45 (s, 2H), 1.28 (m, 3H), 2.6 (m, 1H), 4.1 (m, 2H), 5.9 (m, 1H), 7.68−8.66 (m, 26H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −67.6 (t, J = 11.2 Hz, 2F, −CF_2Cl), −107 to −108 (m, 1F, =CFCF_2−), −109 to −110 (m, 2F, =CFCF_2−), −119 to −120 (m, 2F, −CF_2CF_2Cl). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 658 (2.5), 603 (1), 559 (1.8), 528 (2), 422 (29). MS (EI, relative intensity) *m/z*: 942 (M^+, 37.48). IR (KBr): 3350 (NH), 1751 (−CO_2−), 1185 (CF). Anal. Calcd for $C_{53}H_{35}F_7N_5O_2Cl$: C, 67.55; H, 3.74; N, 7.43; F, 14.11. Found: C, 67.06; H, 4.32; N, 7.17; F, 14.24.

5,10,15,20-Tetraphenyl-2-[bis(cyano)methyl]-3-[1-fluoro-1-(3-chlorohexfluoropropyl)methylenyl]porphrin (7d). Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −1.49 (s, 1H), −1.56 (s, 1H), 4.2 (dd, J_{H-H} = 0.9 Hz, J_{F-H} = 5.6 Hz, 1H), 5.9 (m, 1H), 7.64−8.7 (m, 26H). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): −67.76 (t, J = 11.2 Hz, 2F, −CF_2Cl), −105.88 (m, 1F, =CFCF_2−), −107 to −110.2 (m, 2F, =CFCF_2−), −119.3 to −121.8 (m, 2F, −CF_2CF_2Cl). UV−vis λ_{max} (relative intensity, CH_2Cl_2): 657 (2.5), 603 (1), 560 (1.7), 528 (1.7), 422 (28). MS (MALDI) *m/z*: 895.2 (MH^+). IR (KBr): 3354 (NH), 1188 (CF). Anal. Calcd for $C_{51}H_{30}F_7N_6Cl\cdot 0.5H_2O$: C, 67.74; H, 3.43; N, 9.29. Found: C, 67.98; H, 3.7; N, 8.82.

Acknowledgment. We would like to thank the National Nature Science Foundation of China (29972051, D20032010) for financial support of this work.

Supporting Information Available: ^{1}H and ^{19}F NMR spectra for compounds **3aa**−**dd**, **Zn3aa**−**3db**, **5ad2**, **7a**−**d**, ^{13}C NMR spectra for compounds **3aa** and **7a**, and DEPT NMR spectra for compound **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0207269