

# Fluoroalkylation of porphyrins: Preparation and characterization of *meso*- and $\beta$ -fluoroalkyl-5,15-diarylporphyrins

Li-Mei Jin<sup>a</sup>, Liang Chen<sup>b</sup>, Juan-Juan Yin<sup>c</sup>, Can-Cheng Guo<sup>b,\*</sup>, Qing-Yun Chen<sup>a,b,\*</sup>

<sup>a</sup> Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

<sup>b</sup> College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

<sup>c</sup> Nanobiology Medicine Department, Shanghai Applied Physical Institute, Chinese Academy of Sciences, 2019 Jialuo Road, Shanghai 201800, China

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## Abstract

Treatment of zinc(II) 5,15-diphenylporphyrin or free-base 5,15-diphenylporphyrin with 1.1 eq. of fluoroalkyl iodides ( $R_fI$ ) in the presence of 1.1 eq.  $Na_2S_2O_4$  in a mixture solvent of DMSO/THF at 45 °C for 1–2 h gave 2-fluoroalkyl-5,15-diphenylporphyrin and 5-fluoroalkyl-10,20-diphenylporphyrin in a ratio from 1/3 to 1/8 in almost 50% total yields. The 5-fluoroalkyl-10,20-diphenylporphyrins were further fluoroalkylated to yield bis-fluoroalkylporphyrins.

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## 1. Introduction

*meso*- and  $\beta$ -Fluorinated or perfluoroalkylated porphyrins and metalloporphyrins have been shown to have unique properties in catalysis, materials and medical applications, etc. [1–11]. For example, 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin ligand was successfully used as fluorocarbon soluble sensitizer for the photo-oxidation of allylic alcohols to hydroperoxide under fluorous biphasic system [11]. However, the existing methods based on the condensation of fluoroalkylpyrrole and/or fluoroalkylaldehyde are all limited to synthesize symmetric  $\beta$ -octafluoroalkylporphyrins, *meso*-tetrafluoroalkylporphyrins and 5,15-bis-fluoroalkyl-10,20-diarylporphyrins [12–17]. Moreover, the synthetic procedures were suffered from the tedious separation and low yields. Recently, mono  $\beta$ -fluoroalkyl-*meso*-tetraarylporphyrins were successfully prepared from tetraarylporphyrins and fluoroalkyl iodides under sulfinato-

dehalogenation conditions in our laboratory [18]. To the best of our knowledge, asymmetric *meso*-monofluoroalkylporphyrins have not been yet reported probably due to their synthetic difficulty. Therefore, it is desirable to develop a new method for preparing such kind of fluoroalkyl-substituted porphyrins. According to our previous reports [18–21], fluoroalkylation of 5,15-diarylporphyrin under sulfinatodehalogenation conditions seems to be a proper way for synthesizing asymmetric porphyrins if the position of fluoroalkylation could be controlled. In this paper, we present the synthesis of asymmetric *meso*-monofluoroalkylporphyrins and bisfluoroalkylporphyrins.

## 2. Results and discussion

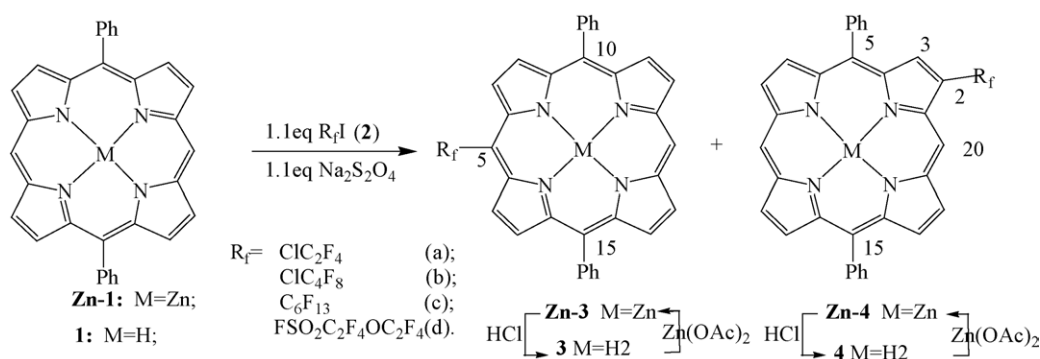
Recently, we have found that the fluoroalkyl groups could be easily introduced onto the  $\beta$  position of the tetraarylporphyrins with fluoroalkyl iodides under sulfinatodehalogenation conditions [18,19]. Using this method, for zincated 5,15-diphenylporphyrin, both *meso*- and  $\beta$ -fluor-

\* Corresponding authors. Tel.: +86 21 54925196; fax: +86 21 64166128.  
E-mail address: [Chenqy@mail.sioc.ac.cn](mailto:Chenqy@mail.sioc.ac.cn) (Q.-Y. Chen).

Table 1  
Fluoroalkylation of 5,15-diphenylporphinato zinc(II)

Entry	Compound	Conditions	Product (yield, %)		Product ratio <sup>a</sup>
1	<b>Zn-1</b>	1.1 eq. <b>2a</b> /1.1 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /1 h	<b>Zn-3a</b> (40)	<b>Zn-4a</b> (10)	4/1
2	<b>Zn-1</b>	1.1 eq. <b>2b</b> /1.1 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /1.5 h	<b>Zn-3b</b> (30)	<b>Zn-4b</b> (10)	3/1
3	<b>Zn-1</b>	1.1 eq. <b>2c</b> /1.1 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /2 h	<b>Zn-3c</b> (40)	<b>Zn-4c</b> (5)	8/1
4	<b>Zn-1</b>	1.1 eq. <b>2d</b> /1.1 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /2 h	<b>Zn-3d</b> (45)	<b>Zn-4d</b> (9)	5/1
5	<b>Zn-1</b>	3 eq. <b>2a</b> /3 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /5 h	<b>Zn-5a</b> (20)	<b>Zn-6a</b> (20)	1/1
6	<b>Zn-3a</b>	1 eq. <b>2a</b> /1 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /1 h	<b>Zn-5a</b> (40)	<b>Zn-6a</b> (40)	1/1
7	<b>Zn-3c</b>	1 eq. <b>2a</b> /1 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /1 h	<b>Zn-5c</b> (40)	<b>Zn-6c</b> (40)	1/1
8	<b>1</b>	1.1 eq. <b>2a</b> /1.1 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /2 h	<b>3a</b> (45)	<b>4a</b> (15)	3/1
9	<b>1</b>	1.1 eq. <b>2c</b> /1.1 eq. Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> /2 h	<b>3c</b> (40)	<b>4c</b> (20)	2/1

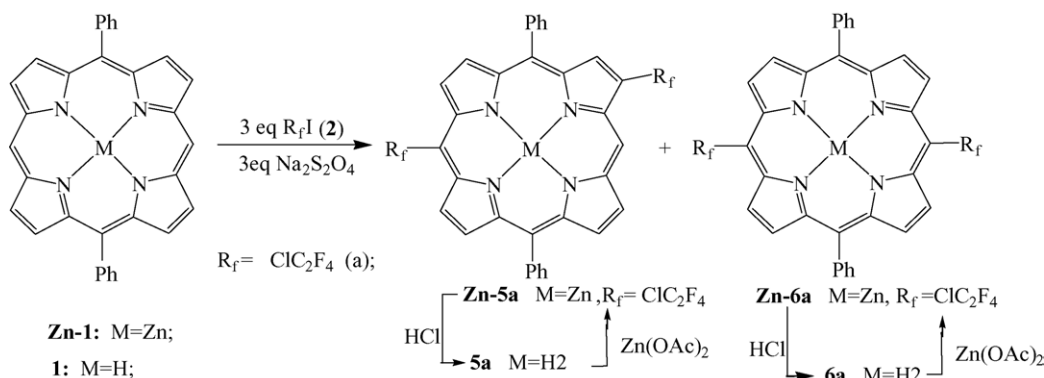
<sup>a</sup> Determined by <sup>1</sup>H and <sup>19</sup>F NMR.



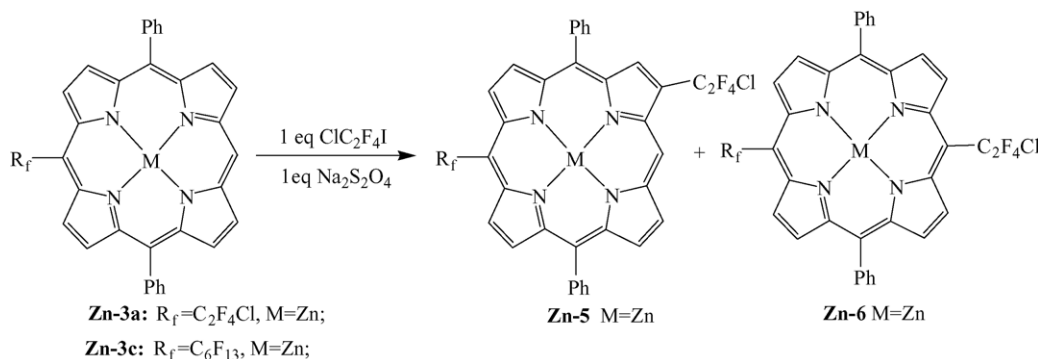
Scheme 1.

oalkylated porphyrins were obtained. Thus, treatment of **Zn-1** [22] with 1.1 eq. R<sub>f</sub>I (**2**) in the presence of 1.1 eq. Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in a mixture solvent of THF/DMSO (1/1, v/v) at 35 °C for about 2 h, followed by demetalation with concentrated HCl (for easy separation of mono-fluoroalkylated product from **1**) yielded not only **3** (50–60%), but also **4** (8–15%), together with a recovery of **1** (20–30%) and trace amount of disubstituted products. However, the polarity of the two isomers **3** and **4** is too close to be separated from each other. Fortunately, when they were metalated again with Zn(OAc)<sub>2</sub>, followed by purification with dry powder column chromatography (300–400 meshes, SiO<sub>2</sub>), the pure **Zn-3** and **Zn-4** were obtained easily. And the zincated products can be converted into corresponding free-bases **3** and **4**

quantitatively with concentrated HCl (Scheme 1 and Table 1). Compounds **3**, **4** and their zinc complexes were fully characterized by <sup>1</sup>H, <sup>19</sup>F NMR, UV–vis spectroscopy and MALDI mass spectrometry. For example, <sup>1</sup>H NMR analysis of **3c** revealed the presence of one *meso*- and eight β-proton signals. Again, the signals at –78.4 ppm in the <sup>19</sup>F NMR spectra (versus CFC-11) indicated that was the *meso*-fluoroalkylation [23]. While for **4c**, <sup>1</sup>H NMR spectra gave two *meso*- and seven β-proton signals and –100.7 ppm in <sup>19</sup>F NMR spectra showed the β-fluoroalkylation [24]. The fact that no correlation peak of the proton of C3–H and C20–H can be found in the NOSEY spectrum indicated that the fluoroalkyl group was attached into the 2-position of the macrocycle. The fluoroalkyl group was located at 2-position,



Scheme 2.



Scheme 3.

not at 3-position, which can be easily understood because the 2-position is the relative least steric. Similar spectroscopic characteristics were found for other  $R_f$  groups. It is noteworthy that the minus NH proton signals of **3** and **4** were obviously different. For **3c**, the NH proton signals gave singlet peak at  $-2.96$  ppm, while for **4c**, the NH proton signals split into two singlet peaks at  $-3.04$  and  $-3.2$  ppm. The same spectroscopic characteristics were also observed for **3a**, **3b**, **3d**, **4a**, **4b** and **4d** (see Section 4).

By contrast to the good selectivity of fluoroalkylation of **Zn-1** in the first *meso* position versus  $\beta$  position, treating **Zn-1** with 3 eq. **2a**, under otherwise the same conditions, gave a mixture of bisfluoroalkylporphyrins. After standard workup, the equal amounts of products **5a** (20%) and **6a** (20%) were separated and fully characterized, respectively (Scheme 2). On the other hand, the similar regio-bisfluoroalkylporphyrins of **Zn-5** and **Zn-6** were also obtained by the reaction of mono-fluoroalkylporphyrins **Zn-3a** or **Zn-3c** with 1 eq. **2a** (Scheme 3). The results clearly showed that the fluoroalkylation of zinc(II) 5-fluoroalkyl-10,20-diphenylporphyrins did not possess any preference for *meso* position versus  $\beta$  position.

The free-base **1** [22], instead of **Zn-1**, reacted with  $R_fI$  also gave similar products **3** and **4**, but the ratio of the  $\beta$ - and *meso*-fluoroalkylation products was slight higher than that results from **Zn-1** and  $R_fI$  (Table 1).

Notably, the regio-selective activity of fluoroalkylation of the first *meso* position of the 5,15-diphenylporphyrin is two to eight times higher than that of  $\beta$  position which is quite similar to the reactivity of the *meso* sites versus  $\beta$  sites in the reaction of diaryl-substituted chlorin and/or oxochlorin with NBS observed by Lindsey and co-workers recently [25]. However, the further fluoroalkylation demonstrated that the remaining *meso* site of the zinc(II) 5-fluoroalkyl-10,20-diphenylporphyrin, compared to the  $\beta$  site, had no preferential selectivity to fluoroalkyl radicals.

### 3. Conclusions

In summary, we have presented a facile method for one-pot synthesis of mono *meso*- and  $\beta$ -fluoroalkylporphyrins

and bis-*meso,meso*- and *meso*, $\beta$ -fluoroalkylporphyrins. Furthermore, by the step-by-step procedures, the various fluoroalkyl groups can be introduced into the peripheral of the porphyrins. So the method demonstrated here provided a useful access to prepare various fluoroalkylated porphyrins which have heretofore been inaccessible.

## 4. Experimental

### 4.1. General

UV-vis spectra was measured using a Varian Cary UV-visible spectrometer in  $\text{CH}_2\text{Cl}_2$ .  $^1\text{H}$  NMR (300 MHz) and  $^{19}\text{F}$  NMR (282 MHz) spectra were recorded on a Bruker 300 spectrometer with tetramethylsilane,  $\text{CDCl}_3$  ( $\delta = 77$ ) and  $\text{CFCl}_3$  ( $\delta = 0$ ) as standard, respectively. MS and HRMS spectra were recorded on a Hewlett-Packard HP-5989A spectrometer or Bruker APEXIII FTICRMS.

### 4.2. Typical procedure for synthesis of *meso*- and $\beta$ -mono fluoroalkylporphyrins

#### 4.2.1. Method A: from zinc(II) 5,15-diphenylporphyrin and fluoroalkyl iodides, exemplified for the reaction of **Zn-1** with $\text{ClC}_2\text{F}_4\text{I}$ (**2a**)

A sample of zinc(II) 5,15-diphenylporphyrin (**Zn-1**, 200 mg, 0.38 mmol),  $\text{ClC}_2\text{F}_4\text{I}$  (110 mg, 0.42 mmol),  $\text{Na}_2\text{S}_2\text{O}_4$  (73 mg, 0.42 mmol) were stirred in DMSO (20 ml) and THF (20 ml) at  $40^\circ\text{C}$  for 3 h. Then,  $\text{CH}_2\text{Cl}_2$  (100 ml) was added and the mixture was washed with ice water several times. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and rotary evaporated to dryness. The crude products were dissolved in  $\text{CH}_2\text{Cl}_2$  (100 ml) and concentrated HCl (2 ml) was added. Then, the mixture was stirred at room temperature for 30 min, washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , purified by dry column chromatography (300–400 meshes  $\text{SiO}_2$ , hexanes/ $\text{CH}_2\text{Cl}_2$ , 3/1, v/v) mainly to yield two fractions. The first fraction gave the mixture of **3a** and **4a** (total weight: 113 mg, 50%).  $^{19}\text{F}$  NMR analysis of the mixture indicated a 4:1 product ratio (**3a** versus **4a**). The second fraction afforded the unconverted

demetalated starting porphyrin **1a** (70 mg, 35%). The isomers (**3a** and **4a**) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 ml), then a solution of Zn(OAc)<sub>2</sub> (417 mg, 1.89 mmol) in CH<sub>3</sub>OH (5 ml) was added. The mixture was stirred at room temperature for 30 min to yield a light purple-red solution. After purified by dry column chromatography (300–400 meshes SiO<sub>2</sub>, hexanes/CH<sub>2</sub>Cl<sub>2</sub>, 1/1, v/v), pure **Zn-3a** (100 mg, 40%) and **Zn-4a** (25 mg, 10%) were obtained, respectively. To a solution of **Zn-3a** (20 mg, 0.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml), concentrated HCl (0.1 ml) was added, then the mixture was stirred at room temperature for 10 min, washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and rotary evaporated to dryness to afford **3a** quantitatively. Similarly, reaction of **Zn-4a** (20 mg, 0.03 mmol) with concentrated HCl (0.1 ml) afforded the free-base **4a** quantitatively.

4.2.2. Method B: from free-base 5,15-diphenylporphyrin and fluoroalkyl iodides, exemplified for the reaction of **1** with ClC<sub>2</sub>F<sub>4</sub>I (**2a**)

A sample of 5,15-diphenylporphyrin (**1**, 100 mg, 0.22 mmol), ClC<sub>2</sub>F<sub>4</sub>I (60 mg, 0.24 mmol), Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (42 mg, 0.24 mmol) was stirred in DMSO (10 ml) and CH<sub>2</sub>Cl<sub>2</sub> (10 ml) at 40 °C for 3 h. Then, CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was added and the mixture was washed with ice water several times. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and rotary evaporated to dryness. The crude products were purified by dry column chromatography (300–400 meshes SiO<sub>2</sub>, hexanes/CH<sub>2</sub>Cl<sub>2</sub>, 3/1, v/v) mainly to yield two fractions. The first fraction gave the mixture of **3a** and **4a** (total weight: 75 mg, 60%). <sup>19</sup>F NMR analysis of the mixture indicated a 3:1 product ratio (**3a** versus **4a**). The second fraction afforded the unconverted starting porphyrin **1** (35 mg, 35%). The isomers (**3a** and **4a**, 75 mg, 0.125 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 ml), then a solution of Zn(OAc)<sub>2</sub> (275 mg, 1.25 mmol) in CH<sub>3</sub>OH (5 ml) was added. The mixture was stirred at room temperature for 30 min to yield a light purple-red solution. After purified by dry powder column chromatography (300–400 meshes SiO<sub>2</sub>, hexanes/CH<sub>2</sub>Cl<sub>2</sub>, 1/1, v/v), the pure **Zn-3a** (58 mg, yield: 95%, based on **3a**) and **Zn-4a** (19 mg, yield: 95%, based on **4a**) were obtained, respectively.

*Zinc(II) 5-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (Zn-3a)*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.765 (s, 1H), 9.68 (brs, 2H), 9.07 (d, *J* = 4.7 Hz, 2H), 9.03 (d, *J* = 4.2 Hz, 2H), 8.82 (d, *J* = 4.5 Hz, 2H), 8.14 (d, *J* = 6.5 Hz, 4H), 7.80 (m, 6H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = -63.38 (s, 2F), -74.66 (s, 2F). ESI-MS: *m/z* 659 [M + H]<sup>+</sup>. UV-vis λ<sub>max</sub>: 410, 542, 576. Anal. calcd. for C<sub>34</sub>H<sub>19</sub>ClF<sub>4</sub>N<sub>4</sub>Zn·H<sub>2</sub>O: C, 60.18; H, 3.1; N, 8.26; found: C, 60.44; H, 3.44; N, 7.8.

*Zinc(II) 5-(4-chlorooctafluorobutyl)-10,20-diphenylporphyrin (Zn-3b)*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.64 (brs, 2H), 9.457 (s, 1H), 9.07 (d, *J* = 5.2 Hz, 2H), 8.83 (d, *J* = 4.2 Hz, 2H), 8.72 (d, *J* = 4.3 Hz, 2H), 8.106 (brs, 4H), 7.82 (m, 6H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = -67.61 (m,

2F), -76.51 (2F, m), -114.24 (m, 2F), -119.35 (m, 2F). ESI-MS: *m/z* 759.15 [M + H]<sup>+</sup>. UV-vis λ<sub>max</sub>: 410, 541, 575. Anal. calcd. for C<sub>36</sub>H<sub>19</sub>ClF<sub>8</sub>N<sub>4</sub>Zn: C, 56.86; H, 2.52; N, 7.37; found: C, 56.69; H, 3.00; N, 7.02.

*Zinc(II) 5-perfluorohexyl-10,20-diphenylporphyrin (Zn-3c)*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.104 (s, 1H), 9.63 (brs, 2H), 9.25 (d, *J* = 4.5 Hz, 2H), 9.09 (d, *J* = 5.2 Hz, 2H), 8.95 (d, *J* = 4.5 Hz, 2H), 8.19 (brs, 4H), 7.81 (m, 6H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = -76.48 (s, 2F), -80.88 (m, 3F), -114.99 (s, 2F), -121.3 (m, 2F), -122.6 (m, 2F), -126.18 (s, 2F). ESI-MS: *m/z* 843.25 [M + H]<sup>+</sup>. UV-vis λ<sub>max</sub>: 410, 542, 576. Anal. calcd. for C<sub>38</sub>H<sub>19</sub>F<sub>13</sub>N<sub>4</sub>Zn: C, 54.08; H, 2.27; N, 6.64; found: C, 54.12; H, 2.48; N, 6.40.

*Zinc(II) 5-(3-oxa-ω-fluorosulfonyl perfluoropentanyl)-10,20-diphenylporphyrin (Zn-3d)*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.211 (s, 1H), 9.645 (brs, 2H), 9.32 (d, *J* = 4.7 Hz, 2H), 9.08 (d, *J* = 5.3 Hz, 2H), 8.98 (d, *J* = 4.5 Hz, 2H), 8.20 (d, *J* = 6.5 Hz, 4H), 7.80 (m, 6H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = 45.52 (s, 1F), -79.7 (s, 2F), -81.29 (m, 2F), -81.9 (s, 2F), -111.76 (s, 2F). MALDI-MS: *m/z* 823.20 [M + H]<sup>+</sup>. UV-vis λ<sub>max</sub>: 410, 541, 575. HRMS (MALDI) calcd. for C<sub>36</sub>H<sub>19</sub>N<sub>4</sub>O<sub>3</sub>F<sub>9</sub>SZn·H<sup>+</sup>, 823.0398, found: 823.0447.

*2-(2-Chlorotetrafluoroethyl)-5,15-diphenylporphyrin (Zn-4a)*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.55 (s, 1H), 10.29 (s, 1H), 9.50 (d, *J* = 4.0 Hz, 1H), 9.42 (m, 3H), 9.13 (d, *J* = 5.2 Hz, 3H), 8.25 (m, 4H), 7.82 (m, 6H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = -68.66 (s, 2F), -99.73 (s, 2F). ESI-MS: *m/z* 659 [M + H]<sup>+</sup>. UV-vis λ<sub>max</sub>: 411, 540, 577. Anal. calcd. for C<sub>34</sub>H<sub>19</sub>ClF<sub>4</sub>N<sub>4</sub>Zn·5.5H<sub>2</sub>O: C, 53.75; H, 3.95; N, 7.37; found: C, 54.08; H, 3.74; N, 6.88.

*Zinc(II) 5-(4-chlorooctafluorobutyl)-10,20-diphenylporphyrin (Zn-4b)*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.515 (s, 1H), 10.266 (s, 1H), 9.50 (d, *J* = 4.6 Hz, 1H), 9.40 (m, 3H), 9.13 (m, 3H), 8.25 (m, 4H), 7.83 (m, 6H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = -67.97 (s, 2F), -100.77 (s, 2F), -119.11 (s, 2F), -119.55 (s, 2F). ESI-MS: *m/z* 759.25 [M + H]<sup>+</sup>. UV-vis λ<sub>max</sub>: 411, 539, 578. HRMS (MALDI) calcd. for C<sub>36</sub>H<sub>19</sub>N<sub>4</sub>F<sub>8</sub>ClZn·H<sup>+</sup>: 759.0535; found, 759.0535.

*Zinc(II) 2-perfluorohexyl-5,15-diphenylporphyrin (Zn-4c)*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.485 (s, 1H), 10.197 (s, 1H), 9.48 (d, *J* = 4.5 Hz, 1H), 9.409 (s, 1H), 9.36 (dd, *J* = 2.7, 2.7 Hz, 2H), 9.10 (m, 3H), 8.24 (m, 4H), 7.82 (m, 6H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = -80.99 (m, 3F), -100.7 (m, 2F), -119.7 (m, 2F), -121.43 (m, 2F), -122.9 (m, 2F), -126.35 (m, 2F). ESI-MS: *m/z* 843.2 [M + H]<sup>+</sup>. UV-vis λ<sub>max</sub>: 411, 540, 576. Anal. calcd. for C<sub>38</sub>H<sub>19</sub>F<sub>13</sub>N<sub>4</sub>Zn: C, 54.08; H, 2.27; N, 6.64; found: C, 54.46; H, 2.49; N, 6.56.

*Zinc(II) 5-(3-oxa-ω-fluorosulfonyl perfluoropentanyl)-10,20-diphenylporphyrin (Zn-4d)*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.488 (s, 1H), 10.143 (s, 1H), 9.46 (d, *J* = 4.5 Hz, 1H), 9.388 (s, 1H), 9.32 (d, *J* = 4.5 Hz, 1H), 9.10 (m, 3H), 8.23 (d, *J* = 7.4 Hz, 4H), 7.82 (m, 6H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = 45.4 (m, 1F), -82.23 (s, 2F), -85.38 (m, 2F), -103.64 (s, 2F), -112.27 (s, 2F). ESI-MS:

$m/z$  823.2  $[M + H]^+$ . UV–vis  $\lambda_{\max}$ : 411, 540, 576. Anal. calcd. for  $C_{36}H_{20}N_4O_3F_9SZn$ : 823.0398, found: 823.0414.

**5-(2-Chlorotetrafluoroethyl)-10,20-diphenylporphyrin (3a)**:  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 10.248 (s, 1H), 9.567 (brs, 2H), 9.30 (d,  $J$  = 4.4 Hz, 2H), 9.00 (d,  $J$  = 5.4 Hz, 2H), 8.91 (d,  $J$  = 4.7 Hz, 2H), 8.21 (d,  $J$  = 6.8 Hz, 4H), 7.79 (m, 6H),  $-2.984$  (s, 2H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ ):  $\delta$  =  $-63.92$  (s, 2F),  $-76.85$  (s, 2F). ESI-MS:  $m/z$  597.25  $[M + H]^+$ . UV–vis  $\lambda_{\max}$ : 410, 507, 538, 579, 632. Anal. calcd. for  $C_{34}H_{21}ClF_4N_4 \cdot 1.5H_2O$ : C, 65.38; H, 3.85; N, 8.97; found: C, 65.41; H, 4.44; N, 8.66.

**5-(4-Chlorooctafluorobutyl)-10,20-diphenylporphyrin (3b)**:  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 10.270 (s, 1H), 9.501 (brs, 1H), 9.30 (d,  $J$  = 4.4 Hz, 2H), 8.99 (d,  $J$  = 5.2 Hz, 2H), 8.91 (d,  $J$  = 4.5 Hz, 2H), 8.20 (d,  $J$  = 7.1 Hz, 4H), 7.80 (m, 6H),  $-2.969$  (s, 2H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ ):  $\delta$  =  $-67.7$  (m, 2F),  $-78.4$  (m, 2F),  $-114.5$  (s, 2F),  $-119.3$  (m, 2F). ESI-MS:  $m/z$  697.3  $[M + H]^+$ . UV–vis  $\lambda_{\max}$ : 409, 507, 541, 578, 632. Anal. calcd. for  $C_{36}H_{21}ClF_8N_4 \cdot 3.5H_2O$ , calcd.: C, 56.84; H, 3.68; N, 7.37; found: C, 56.65; H, 3.10; N, 7.12.

**5-Perfluorohexyl-10,20-diphenylporphyrin (3c)**:  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 10.276 (s, 1H), 9.52 (brs, 2H), 9.31 (d,  $J$  = 4.4 Hz, 2H), 9.01 (d,  $J$  = 5.5 Hz, 2H), 8.92 (d,  $J$  = 5.0 Hz, 2H), 8.21 (d,  $J$  = 6.9 Hz, 4H), 7.82 (m, 6H),  $-2.964$  (s, 2H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ ):  $\delta$  =  $-78.42$  (s, 2F),  $-80.90$  (s, 3F),  $-115.32$  (s, 2F),  $-121.31$  (s, 2F),  $-122.61$  (s, 2F),  $-126.15$  (s, 2F). ESI-MS:  $m/z$  781.05  $[M + H]^+$ . UV–vis  $\lambda_{\max}$ : 409, 507, 538, 578, 632. Anal. calcd. for  $C_{38}H_{21}F_{13}N_4$ : C, 58.47; H, 2.71; N, 7.18; found: C, 57.62; H, 2.79; N, 6.81.

**5-(3-Oxa- $\omega$ -fluorosulfonyl perfluoropentanyl)-10,20-diphenylporphyrin (3d)**:  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 10.282 (s, 1H), 9.529 (brs, 1H), 9.32 (d,  $J$  = 4.4 Hz, 2H), 9.01 (d,  $J$  = 4.7 Hz, 2H), 8.92 (d,  $J$  = 4.5 Hz, 2H), 8.21 (d,  $J$  = 7.4 Hz, 4H), 7.82 (m, 6H),  $-2.982$  (s, 2H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ ):  $\delta$  = 45.57 (s, 1F),  $-81.70$  (m, 6F),  $-111.84$  (s, 2F). ESI-MS:  $m/z$  761.05  $[M + H]^+$ . UV–vis  $\lambda_{\max}$ : 409, 507, 539, 578, 633. Anal. calcd. for  $C_{36}H_{21}F_9N_4O_3S$ : C, 56.85; H, 2.78; N, 7.37; found: C, 57.28; H, 3.56; N, 7.18.

**5-(4-Chlorooctafluorobutyl)-10,20-diphenylporphyrin (4b)**:  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 10.520 (s, 1H), 10.308 (s, 1H), 9.55 (d,  $J$  = 4.8 Hz, 1H), 9.47 (d,  $J$  = 4.9 Hz, 1H), 9.32 (d,  $J$  = 3.9 Hz, 2H), 9.16 (d,  $J$  = 4.9 Hz, 2H), 9.01 (d,  $J$  = 4.5 Hz, 1H), 8.27 (m, 4H), 7.84 (m, 6H),  $-3.04$  (s, 1H),  $-3.20$  (s, 1H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ ):  $\delta$  =  $-67.97$  (s, 2F),  $-100.7$  (m, 2F),  $-119.07$  (s, 2F),  $-119.45$  (s, 2F). ESI-MS:  $m/z$  697.15  $[M + H]^+$ . UV–vis  $\lambda_{\max}$ : 410, 509, 541, 581, 634. HRMS (MALDI) calcd. for  $C_{36}H_{22}N_4ClF_8$ : 697.1400, found: 697.1407.

**2-Perfluorohexyl-5,15-diphenylporphyrin (4c)**:  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 10.47 (s, 1H), 10.13 (s, 1H), 9.47 (d,  $J$  = 4.8 Hz, 1H), 9.40 (s, 1H), 9.31 (dd,  $J$  = 2.1, 2.3 Hz, 2H), 9.09 (m, 3H), 8.23 (m, 4H), 7.82 (m, 6H),  $-3.04$  (s, 1H),  $-3.19$  (s, 1H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ ):  $\delta$  =  $-81.00$  (s,

3F),  $-100.7$  (m, 2F),  $-119.75$  (s, 2F),  $-121.39$  (s, 2F),  $-122.89$  (s, 2F),  $-126.34$  (s, 2F). ESI-MS:  $m/z$  781.1  $[M + H]^+$ . UV–vis  $\lambda_{\max}$ : 410, 507, 542, 580, 636. HRMS (MALDI) calcd. for  $C_{38}H_{21}N_4F_{13}H^+$ : 781.1631; found, 781.1657.

**5-(3-Oxa- $\omega$ -fluorosulfonyl perfluoropentanyl)-10,20-diphenylporphyrin (4d)**:  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 10.529 (s, 1H), 10.297 (s, 1H), 9.54 (d,  $J$  = 4.8 Hz, 1H), 9.46 (d,  $J$  = 4.9 Hz, 1H), 9.31 (d,  $J$  = 3.1 Hz, 2H), 9.17 (d,  $J$  = 4.3 Hz, 2H), 9.01 (d,  $J$  = 4.5 Hz, 1H), 8.25 (m, 4H), 7.87 (m, 6H),  $-3.047$  (s, 1H),  $-3.195$  (s, 1H).  $^{19}F$  NMR (282 MHz,  $CDCl_3$ ):  $\delta$  = 45.46 (s, 1F),  $-82.20$  (s, 2F),  $-85.29$  (s, 2F),  $-103.4$  (s, 2F),  $-112.26$  (s, 2F). ESI-MS:  $m/z$  761.05  $[M + H]^+$ . UV–vis  $\lambda_{\max}$ : 410, 509, 581, 634. Anal. calcd. for  $C_{36}H_{21}F_9N_4O_3S$ : C, 56.85; H, 2.78; N, 7.37; found: C, 56.82; H, 3.33; N, 7.18.

### 4.3. Synthesis of bisfluoroalkylporphyrins 5a and 6a

#### 4.3.1. Method A: from Zn-1

A sample of zinc(II) 5,15-diphenylporphyrin (**Zn-1**, 105 mg, 0.2 mmol),  $ClC_2F_4I$  (**2a**, 0.6 mmol),  $Na_2S_2O_4$  (104 mg, 0.6 mmol) were stirred in DMSO (20 ml) and THF (20 ml) at 40 °C for 5 h. Then,  $CH_2Cl_2$  (100 ml) was added and the mixture was washed with ice water several times. The organic layer was dried over anhydrous  $Na_2SO_4$  and rotary evaporated to dryness. The crude products were dissolved in  $CH_2Cl_2$  (100 ml) and concentrated HCl (5 ml) was added. Then, the mixture was stirred at room temperature for 30 min, washed with water, dried over anhydrous  $Na_2SO_4$ , purified by flash column chromatography (300–400 meshes  $SiO_2$ , hexanes/ $CH_2Cl_2$ , 10/1, v/v) mainly to yield two fractions. The first fraction afforded the **5a** (29 mg, 20%). The second fraction gave the **6a** (29 mg, 20%).

#### 4.3.2. Method B: from Zn-3a

A sample of zinc(II) 5-(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (**Zn-3a**, 40 mg, 0.06 mmol),  $ClC_2F_4I$  (**2a**, 0.06 mmol),  $Na_2S_2O_4$  (11 mg, 0.06 mmol) were stirred in DMSO (2 ml) and THF (2 ml) at 40 °C for 1 h. Then,  $CH_2Cl_2$  (30 ml) was added and the mixture was washed with ice water several times. The organic layer was dried over anhydrous  $Na_2SO_4$  and rotary evaporated to dryness. The crude products were dissolved in  $CH_2Cl_2$  (30 ml) and concentrated HCl (1 ml) was added. Then, the mixture was stirred at room temperature for 30 min, washed with water, dried over anhydrous  $Na_2SO_4$ , purified by flash column chromatography (300–400 meshes  $SiO_2$ , hexanes/ $CH_2Cl_2$ , 10/1, v/v) mainly to yield two fractions. The first fraction afforded the **5a** (17 mg, 40%). The second fraction gave the **6a** (17 mg, 40%).

**2,10-Bis(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (5a)**:  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 10.509 (s, 1H), 9.635 (brs, 1H), 9.46 (d,  $J$  = 4.8 Hz, 2H), 9.155 (s, 1H), 9.09 (d,  $J$  = 5.4 Hz, 2H), 9.00 (d,  $J$  = 4.7 Hz, 1H), 8.91 (d,

$J = 5.0$  Hz, 1H), 8.21 (m, 4H), 7.83 (m, 6H),  $-2.82$  (brs, 2H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta = -64.07$  (s, 2F),  $-68.82$  (s, 2F),  $-77.33$  (s, 2F),  $-100.15$  (s, 2F). ESI-MS:  $m/z$  731.2  $[\text{M} + \text{H}]^+$ . UV-vis  $\lambda_{\text{max}}$ : 411, 512, 548, 586, 642. HRMS (MALDI) calcd. for  $\text{C}_{36}\text{H}_{20}\text{N}_4\text{F}_8\text{Cl}_2 \cdot \text{H}^+$ : 731.1010; found: 731.0994.

*5,15-Bis(2-chlorotetrafluoroethyl)-10,20-diphenylporphyrin (6a)*:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.519$  (s, 4H), 8.90 (m, 4H), 8.18 (d,  $J = 7.1$  Hz, 4H), 7.81 (m, 6H),  $-2.468$  (s, 2H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta = -64.52$  (s, 2F),  $-80.11$  (s, 2F). ESI-MS:  $m/z$  731.15  $[\text{M} + \text{H}]^+$ . UV-vis  $\lambda_{\text{max}}$ : 410, 511, 549, 592, 646. Anal. calcd. for;  $\text{C}_{36}\text{H}_{20}\text{Cl}_2\text{F}_8\text{N}_4 \cdot 2\text{H}_2\text{O}$ , C, 56.32; H, 3.13; N, 7.30; found: C, 56.14; H, 2.77; N, 7.09.

*Zinc(II) 2,10-bis(2-chlorotetrafluoroethyl)-5,15-diphenylporphyrin (Zn-5a)*: The title compound was obtained by the reaction of **5a** (10 mg, 0.014 mmol) and  $\text{Zn}(\text{OAc})_2$  (30 mg, 0.14 mmol) in 95% yield.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 10.537$  (s, 1H), 9.643 (s, 2H), 9.45 (d,  $J = 4.5$  Hz, 1H), 9.278 (s, 1H), 9.06 (d,  $J = 4.6$  Hz, 2H), 9.00 (d,  $J = 4.9$  Hz, 1H), 8.19 (m, 4H), 7.82 (m, 6H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta = -63.53$  (s, 2F),  $-68.75$  (s, 2F),  $-74.83$  (s, 2F),  $-99.88$  (s, 2F). MALDI-MS:  $m/z$  793.3  $[\text{M} + \text{H}]^+$ . UV-vis  $\lambda_{\text{max}}$ : 414, 546, 584. HRMS (MALDI) calcd. for  $\text{C}_{36}\text{H}_{18}\text{N}_4\text{F}_8\text{Cl}_2\text{Zn} \cdot \text{H}^+$ : 793.0145; found: 793.0156.

*2-(2-Chlorotetrafluoroethyl)-10-perfluorohexyl-5,15-diphenylporphyrin (5c)* and *5-(2-chlorotetrafluoroethyl)-15-perfluorohexyl-10,20-diphenylporphyrin (6c)*: Following the same procedure for **5a** and **6a** described in Method B, the title compounds were obtained from the reaction of **Zn-3c** (100 mg, 0.12 mmol),  $\text{ClC}_2\text{F}_4\text{I}$  (35 mg, 0.13 mmol) and  $\text{Na}_2\text{S}_2\text{O}_4$  (23 mg, 0.13 mmol) in DMSO (10 ml) and THF (10 ml) as a purple solid after chromatography (silica gel,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 1/20, v/v).

**5c** (44 mg, 40%)  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.51$ – $9.45$  (m, 4H),  $8.92$ – $8.89$  (m, 4H),  $8.17$ – $8.15$  (m, 4H),  $7.87$ – $7.76$  (m, 6H),  $-2.51$  (s, 2H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta = -64.62$  (m, 2F),  $-80.14$  (m, 2F),  $-81.03$  (m, 3F),  $-81.78$  (m, 2F),  $-115.80$  (m, 2F),  $-121.36$  (m, 2F),  $-122.81$  (m, 2F),  $-126.32$  (m, 2F). ESI-MS:  $m/z$  915.2  $[\text{M} + \text{H}]^+$ . UV-vis  $\lambda_{\text{max}}$ : 412, 512, 550, 584, 638. Anal. calcd. for  $\text{C}_{40}\text{H}_{22}\text{ClF}_{17}\text{N}_4\text{O} \cdot \text{H}_2\text{O}$ : C, 51.49; H, 2.38; N, 6.00; found: C, 51.47; H, 2.60; N, 5.74.

**6c** (44 mg, 40%)  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 10.49$  (s, 1H),  $9.57$ – $9.55$  (m, 1H),  $9.45$  (d,  $J = 4.6$  Hz, 1H),  $9.38$  (m, 1H),  $9.13$  (s, 1H),  $9.07$  (d,  $J = 5.1$  Hz, 1H),  $8.99$  (d,  $J = 4.9$  Hz, 1H),  $8.89$  (d,  $J = 5.0$  Hz, 1H),  $8.19$  (m, 4H),  $7.87$ – $7.78$  (m, 6H),  $-2.85$  (s, 2H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta = -68.97$  (m, 2F),  $-79.03$  (m, 2F),  $-81.02$  (m, 3F),  $-100.31$  (m, 2F),  $-115.45$  (m, 2F),  $-121.40$  (m, 2F),

$-122.74$  (m, 2F),  $-126.29$  (m, 2F). ESI-MS:  $m/z$  915.2  $[\text{M} + \text{H}]^+$ . UV-vis  $\lambda_{\text{max}}$ : 410, 512, 548, 590, 646.

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## References

- [1] E.R. Birnbaum, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, H.B. Gray, *Inorg. Chem.* 34 (1995) 1751–1755.
- [2] S. Camestrini, G. Lora, U. Tonellato, *Tetrahedral Lett.* 42 (2001) 7045–7048.
- [3] E.K. Woller, S.G. DiMagno, *J. Org. Chem.* 62 (1997) 1588–1593.
- [4] S.G. DiMagno, A.K. Wertsching, G.R. Ross, *J. Am. Chem. Soc.* 117 (1995) 8279–8280.
- [5] T. Takeuchi, H.B. Gray, W.A. Goddard, *J. Am. Chem. Soc.* 116 (1994) 9730–9732.
- [6] K.T. Moore, J.T. Fletcher, M.J. Therien, *J. Am. Chem. Soc.* 121 (1999) 5196–5209.
- [7] M. Taniguchi, D. Ra, G. Mo, T. Balasubramanian, J.S. Lindsey, *J. Org. Chem.* 66 (2001) 7342–7354.
- [8] G. Pozzi, F. Montanari, S. Quici, *Chem. Commun.* (1997) 69–70.
- [9] K.M. Barkigia, P. Battioni, V. Riou, D. Mansuy, J. Fajer, *Chem. Commun.* (2002) 956–957.
- [10] K. Aoyagi, H. Toi, Y. Aoyama, H. Ogoshi, *Chem. Lett.* (1988) 1891–1894.
- [11] S.G. DiMagno, P.H. Dussault, J.A. Schultz, *J. Am. Chem. Soc.* 118 (1996) 5312–5313.
- [12] K.M. Smith, in: M. Sainsbury (Ed.), *Rodd's Chemistry of Carbon Compounds*, Suppl. to vol. IVB, Elsevier, Amsterdam, 1997, pp. 277–357 (Chapter 12).
- [13] M. Homma, K. Aoyagi, Y. Aoyama, H. Ogoshi, *Tetrahedron Lett.* 24 (1983) 4343–4346.
- [14] T.P. Wijesekera, *Can. J. Chem.* 74 (1996) 1868–1871.
- [15] J.G. Goll, K.T. Moore, A. Ghosh, M.J. Therien, *J. Am. Chem. Soc.* 118 (1996) 8344–8354.
- [16] S.G. DiMagno, R.A. Williams, M.J. Therien, *J. Org. Chem.* 59 (1994) 6943–6948.
- [17] R.W. Kaesler, E. LeGoff, *J. Org. Chem.* 47 (1982) 5243–5246.
- [18] L.M. Jin, Z. Zeng, C.C. Guo, Q.Y. Chen, *J. Org. Chem.* 68 (2003) 3912–3916.
- [19] Z. Zeng, C. Liu, L.M. Jin, C.C. Guo, Q.Y. Chen, *Eur. J. Org. Chem.* (2005) 306–316.
- [20] L.M. Jin, L. Chen, C.C. Guo, Q.Y. Chen, *J. Porphyrins Phthalocyanines* 9 (2005) 109–120.
- [21] L. Chen, L.M. Jin, C.C. Guo, Q.Y. Chen, *Synlett* (2005) 963–970.
- [22] S.G. DiMagno, V.S.Y. Lin, M.J. Therien, *J. Org. Chem.* 58 (1993) 5983–5993.
- [23] The same characteristic chemical shift of  $\text{CF}_2\text{R}'_f$  attached onto the *meso* position was given in Ref. [14].
- [24] The characteristic chemical shift of  $\text{CF}_2\text{R}'_f$  attached onto the  $\beta$  position was given in Ref. [18].
- [25] M. Taniguchi, M.N. Kim, D. Ra, J.S. Lindsey, *J. Org. Chem.* 70 (2005) 275–285.