β-Perfluoroalkylated *meso*-Aryl-Substituted Subporphyrins: Synthesis and Properties

Shuai Zhao, Chao Liu, Yong Guo, Ji-Chang Xiao, Qing-Yun Chen*

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, 200032, Shanghai, P. R. of China
Fax +86(21)64166128; E-mail: chenqy@sioc.ac.cn

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Abstract: A convenient and effective synthesis of various novel β-perfluoroalkylated subporphyrins has been developed. β-Trifluoromethylated subporphyrins were efficiently synthesized by the reaction of brominated subporphyrins with $FSO_2CF_2CO_2Me$/CuI [with or without $Pd(dba)_2$]. Potentially valuable β-perfluoroalkylated, β-monotetrafluorobenzo, and β-monotrifluorobenzo subporphyrins were successfully obtained by a modified sulfinatodehalogenation reaction. Photophysical and electrochemical studies on several typical perfluoroalkylated subporphyrins demonstrated that β-hexakis-trifluoromethylated subporphyrins show an obviously red-shifted UV/Vis absorption band that arises from macrocycle nonplanar distortion induced by trifluoromethyl groups, but this distortion is not so severe as that of the corresponding β-octakis(trifluoromethyl)-*meso*-tetraphenylporphyrin. This was supported by their redox potential data. In addition, β-monotrifluorobenzo subporphyrin exhibits a special fluorescence spectrum of vibronic structure.

Key words: subporphyrin, palladium, perfluoroalkyl, trifluoromethylation, sulfinatodehalogenation

In recent years, subporphyrin, as a genuine ring-contracted porphyrin, has emerged as an interesting functional pigment due to its unique properties, such as its intense Soret-like absorption band, bright green fluorescence, C_3-molecular symmetry, bowl-shaped 14π-electron aromatic macrocycle.[1–4] The groups of Osuka and Kobayashi reported the synthesis of *meso*-aryl-substituted subporphyrins independently in 2007.[2] Intensive research has now been performed on their functionalization and properties.[3] Although much progress has been achieved, the chemistry of subporphyrins remains greatly unexplored, compared to that of subphthalocyanines.[5]

It is well-known that the properties of subporphyrins, like porphyrins, can be conveniently tuned by peripheral fabrications.[3] Due to the small rotational barriers of *meso*-aryl substituents in *meso*-aryl subporphyrins, they show extremely substituent-dependent optical properties.[2b] Developing new synthetic methods to introduce various functional groups into the periphery of subporphyrins is therefore important to study and understand the properties of subporphyrins.[3g,h] Perfluoroalkyl groups are a class of unique electron-withdrawing substituent because they are inert and strongly σ-electron withdrawing, but do not function as π-electron donors. Their introduction into the periphery of porphyrins has great and special effect on the properties of the ligands.[6] Taking advantage of versatile methods developed by our group for the introduction of perfluoroalkyl groups into the periphery of porphyrins,[7] we synthesized and characterized perfluoroalkylated subporphyrins and herein we present the results.

For the synthesis of the starting *meso*-triaryl subporphyrins, we utilized the synthetic protocol of the Osuka group, which is based on the condensation of pyridine-tri-*N*-pyrrolylborane (PPB) and an aromatic aldehyde.[2b,3c,g]

It should be mentioned that the separation and purification of subporphyrins by this route are tedious and time-consuming owing to the complexity of the reaction and relatively instability of subporphyrins. The introduction of a suitable axial substituent to the center boron is crucial for the successful isolation and characterization of subporphyrins. As reported,[2b] subporphyrins are formed mainly as boron–hydroxy forms during the condensation reaction, which can be readily converted into their boron–methoxy form. The boron–methoxy form is more stable than the boron–hydroxy form and can be isolated. However, in our hands, some boron–methoxy subporphyrins were still not sufficiently stable for the common isolation conditions, resulting in lower isolated yields. When treating an axially hydroxy-substituted subporphyrin with boron trifluoride–diethyl ether complex (20 equiv) in dichloromethane for five minutes, the boron–fluoride subporphyrin was produced in almost quantitative yield (Scheme 1), which is consistent with the literature.[4b] This boron–fluoride subporphyrin was more stable and less polar on silica gel columns, making its isolation more convenient and efficient. In the following studies, all the subporphyrins were transformed into the corresponding boron–fluoride form as the starting material for easy isolation and characterization. In addition, ^{19}F NMR spectra of these boron–fluoride subporphyrins showed an obviously upfield-shifted signal at δ = –157.1, compared to the common boron–fluoride species, such as boron trifluoride–diethyl ether complex (δ = –152.8), which may be due to the shielding effect of the subporphyrin macrocycle.

Next, we attempted to prepare various brominated subporphyrins. For monobromosubporphyrins, *N*-bromosuccinimide was chosen as the brominating reagent.[3h] It was found that the conversion and yield were quite sensitive to the reaction conditions (Table 1). As can be seen in Table 1, with 1.1 equivalents of *N*-bromosuccinimide in a mixture solvent 1,2-dichloromethane–methanol at reflux for

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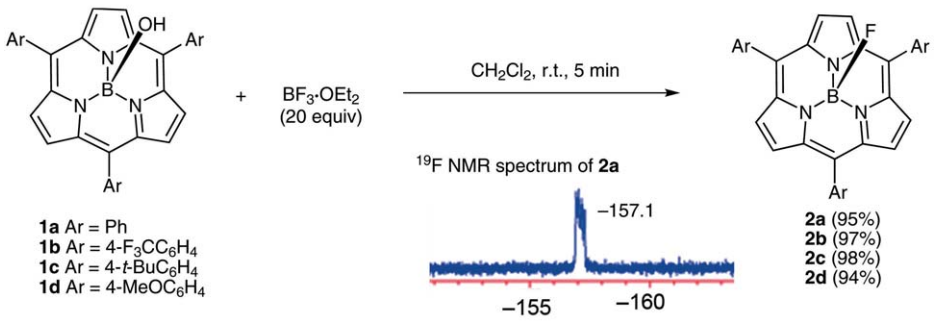
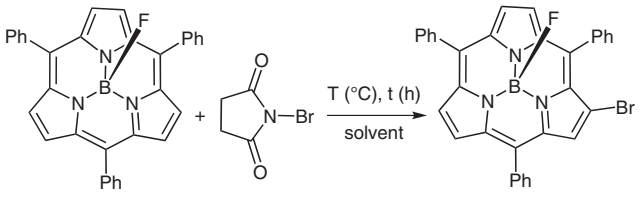


Scheme 1 Axial substituent exchange from B–OH to B–F

two hours (entry 6), the desired subporphyrin **3a** was obtained in good yield (91%), the other *meso*-aryl subporphyrins can also be monobrominated under the optimized conditions to give **3b**,**d** in good yields (Scheme 2). The β-hexabrominated subporphyrins **4a–c** were prepared according to the literature.[3g] Treatment of *meso*-triarylsubporphyrins **2a–c** with bromine at room temperature for ca. 2–3 hours afforded **4a** in 95%, **4b** in 82%, and **4c** in quantitative yields, respectively (Scheme 2).

Table 1 Monobromination Reaction of **2a** under Various Conditions[a]



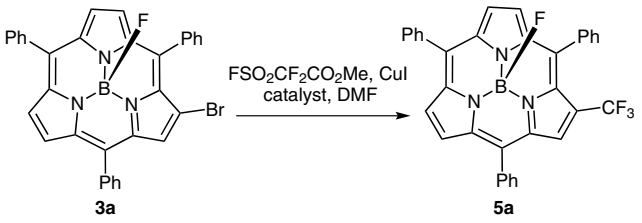
Entry	NBS (equiv)	Solvent	Temp	Time (h)	Conv. (%)	Yield [b] (%)
1	1.1	$CHCl_3$	r.t.	2.5	50	40
2	1.1	$CHCl_3$–MeOH (9:1)	r.t.	2	60	50
3	1.1	$CHCl_3$	reflux	2	82	68
4	1.1	DCE	reflux	2	85	83
5	1.5	DCE	reflux	2	100	73[c]
6	1.1	DCE–MeOH (9:1)	reflux	2	95	91

[a] Reaction conditions: subporphyrin **2a** (20 mg, 40.9 mmol), NBS, solvent (8 mL), stirring, N_2.
[b] Isolated yields based on consumed starting subporphyrin.
[c] 20% of dibrominated product was observed.

With monobrominated and hexabrominated subporphyrins in hand, we examined their trifluoromethylation reactions. Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate ($FSO_2CF_2CO_2Me$), a general trifluoromethylation reagent developed by our group,[8] was used for the trifluoromethylation of brominated subporphyrins; it has been shown to be an excellent trifluoromethylation reagent for the synthesis of various trifluoromethyl-substituted porphyrins in good-to-excellent yields.[7b] It should be noted that a catalytic amount of palladium is necessary for the successful trifluoromethylation of brominated porphyrins, demonstrating that the carbon–bromine bond in porphyrins is more inert than that of normal aromatic bromides, probably due to higher steric hindrance.[7b]

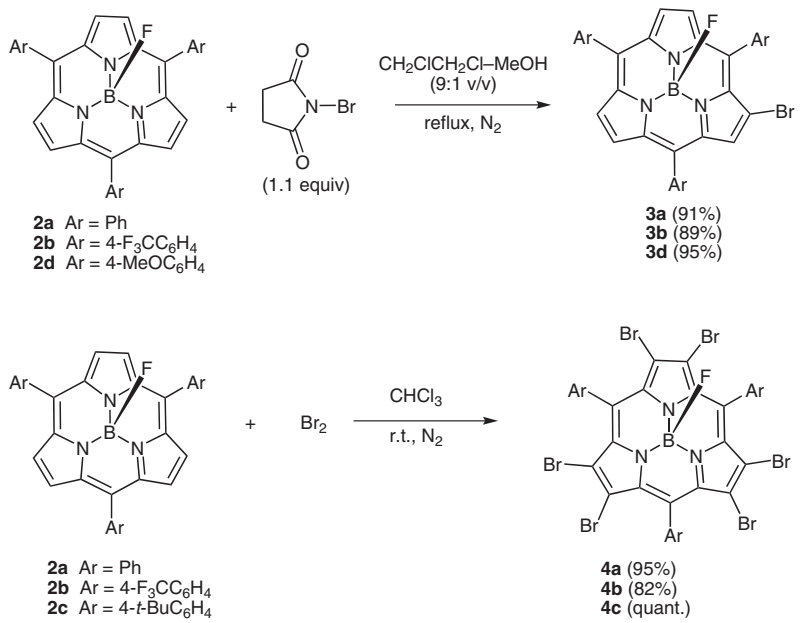
As shown in Table 2, the trifluoromethylation reactions of subporphyrins were conducted under various conditions. It was found that monobromosubporphyrin **3a** was more easily trifluoromethylated than its porphyrin counterpart, but harder than bromobenzene. In the absence of a palladium catalyst, monotrifluoromethylated subporphyrin **5a** was generated in moderate yield, although a longer reaction time was required (entries 1 and 2). As a comparison, bromobenzene was smoothly trifluoromethylated with methyl 2,2-difluoro-2-(fluorosulfonyl)acetate and copper(I) iodide at 80 °C[8] and monobromoporphyrin could not be trifluoromethylated without a palladium catalyst under the similar conditions.[7b] An elevated temperature and using 20 equivalents of methyl 2,2-difluoro-2-(fluo-

Table 2 Trifluoromethylation of β-Monobromosubporphyrin under Various Conditions[a]



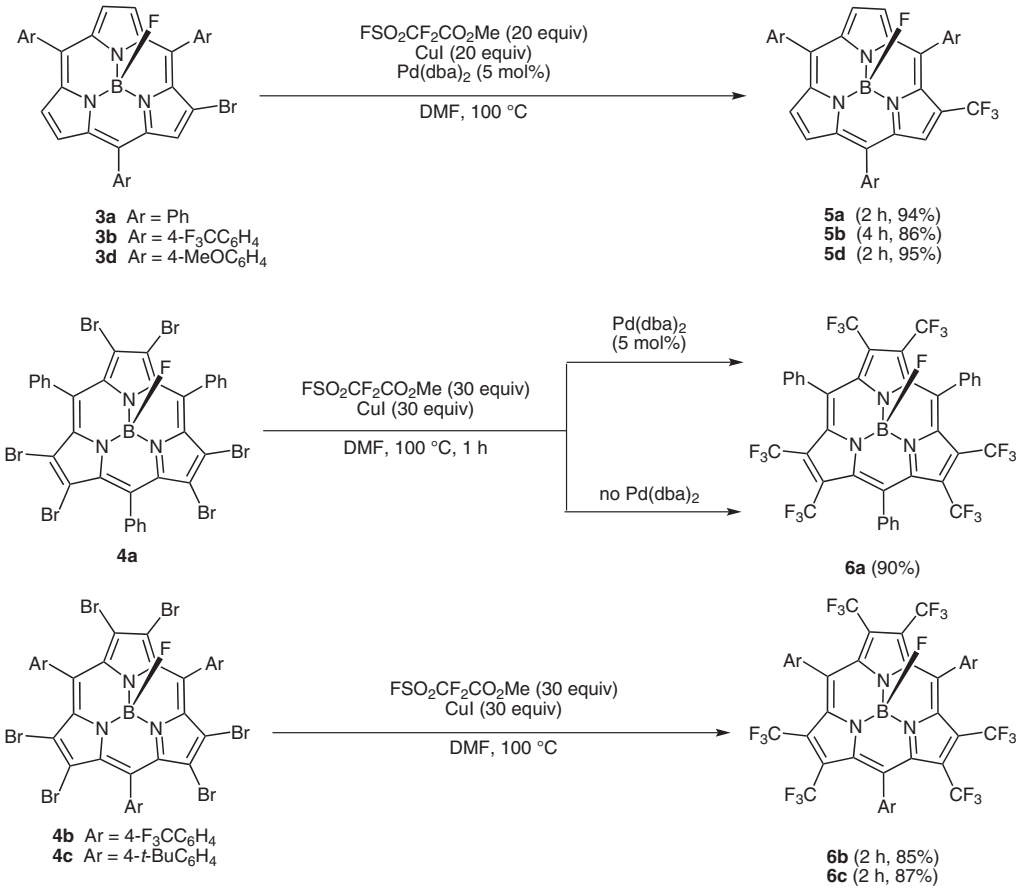
Entry	$FSO_2CF_2CO_2Me$/CuI (equiv)	Catalyst	Temp (°C)	Time (h)	Yield[b] (%)
1	5:5	none	100	6	60
2	10:10	none	100	8	72
3	10:10	$Pd(dba)_2$	100	3	81
4	10:10	$Pd(PPh_3)_4$	100	4	74
5	5:5	$Pd(dba)_2$	100	3	80
6	10:10	$Pd(dba)_2$	80	8	55
7	20:20	$Pd(dba)_2$	100	2	94

[a] Reaction conditions: **3a** (20 mg, 35 mmol), FSO_2CF_2COOMe/CuI, catalyst (5 mol%), DMF (4 mL), N_2.
[b] Isolated yields.



Scheme 2 Mono- and hexabromination of various subporphyrins

rosulfonyl)acetate and copper(I) iodide seemed to be necessary for effective transformation, because lower yields of the desired product were produced at low temperatures even after a longer time (entry 6) or with only five equivalents of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate and copper(I) iodide as the trifluoromethylation reagent (entry 5). With 20 equivalents of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate and copper(I) iodide and $Pd(dba)_2$



Scheme 3 Synthesis of various β-trifluoromethylated subporphyrins

as the catalyst at 100 °C for only two hours, the monotrifluoromethylsubporphyrin **5a** was effectively produced in excellent yield (entry 7).

Under the optimized conditions, various monobromosubporphyrins were subjected to trifluoromethylation, leading to good yields of the desired products (Scheme 3). When β-hexabromosubporphyrins were used as the substrates under the optimized conditions, the corresponding β-hexakistrifluoromethylated subporphyrins **6a–c** were obtained in good yields. It is worth mentioning that in this case, the use of a palladium catalyst was not necessary, since the same yield of the desired product was obtained in the absence of a palladium catalyst (Scheme 3). This shows that it is easier to break C–Br bonds in β-hexabromosubporphyrins, which might be due to the unique bowl-shaped structure of subporphyrins. In addition, the introduction of a strong electron-withdrawing trifluoromethyl group is beneficial to the breaking of residual C–Br bonds as well. As a result, β-hexabromosubporphyrins were readily trifluoromethylated even without a palladium catalyst.

Figure 1 displays ^{1}H NMR spectra of starting subporphyrin **2a**, β-hexabromosubporphyrin **4a**, and β-hexakis(trifluoromethyl)subporphyrin **6a**. The ^{1}H NMR spectrum of *meso*-triphenylsubporphyrin **2a** exhibits an obvious singlet of β-protons at δ = 8.20 and *ortho*-, *meta*-, and *para*-phenyl protons at δ = 8.09, 7.73, and 7.64, respectively. At room temperature, the ^{1}H NMR spectrum of β-hexabromosubporphyrin **4a** shows that the β-protons disappear and rotation of the *meso*-phenyl substituents are restricted. The *ortho*-phenyl protons (δ = 8.10 and 7.31) and *meta*-phenyl protons (δ = 7.72 and 7.52) exhibit broad, but distinctly split, signals. However, at –40 °C, a pair of sharp doublets at δ = 8.12 and 7.25 (*o*-H_{Ph}) and a pair of triplets at δ = 7.75 and 7.51 (*m*-H_{Ph}) are observed. These results are consistent to those in the recent report.[3g] To our surprise, the *ortho*- and *meta*-phenyl protons of β-hexakistrifluoromethylated subporphyrin **6a** exhibit a sharp doublet (δ = 7.79) and a triplet (δ = 7.62) at room temperature, although the trifluoromethyl group has larger steric hindrance than bromine atom. We propose that macrocycle nonplanar distortion stemming from steric congestion of the trifluoromethyl groups might create more spatial spaces for *meso*-phenyl substituents, which lets the *meso*-phenyl substituents rotate more freely.

For the synthesis of β-perfluoroalkylated subporphyrins, the sulfinatodehalogenation was found to be a suitable method, by which various monoperfluoroalkylated porphyrins were prepared.[7c,d] Treatment of subporphyrin **2a** with 4-chloroperfluorobutyl iodide (**7b**) in the presence of sodium dithionite and sodium bicarbonate in a solvent mixture of dimethyl sulfoxide–dichloromethane (1:1) at 35 °C for six hours, successfully afforded the corresponding β-monoperfluoroalkylate subporphyrin **8b**, despite its relatively low yield (Table 3, entry 1). Elevated tempera-

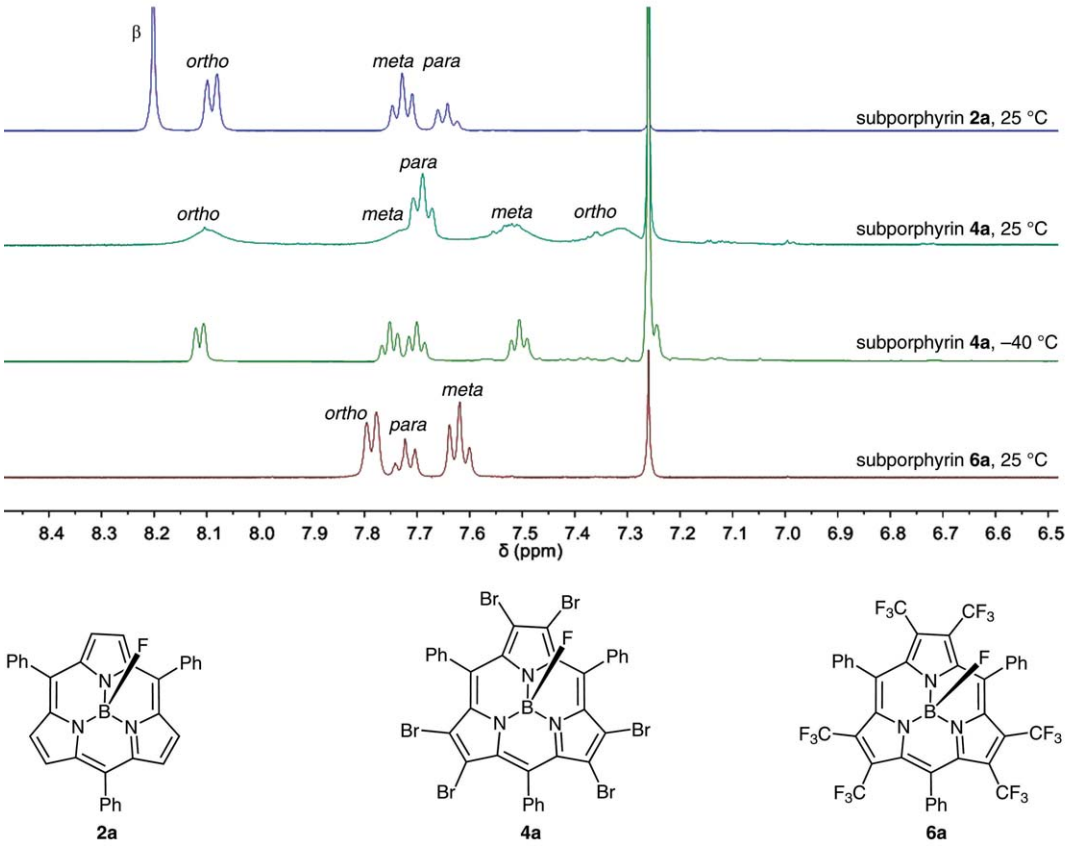
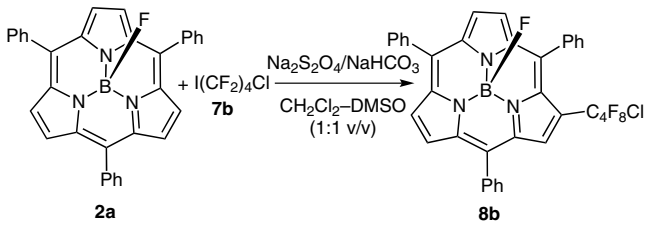


Figure 1 Variable-temperature ^{1}H NMR spectra of **2a**, **4a**, and **6a** in $CDCl_3$

Table 3 Trifluoromethylation of β-Monobromosubporphyrin under Various Conditions[a]



2a **8b**

Entry	$I(CF_2)_4Cl$ (equiv)	$Na_2S_2O_4/NaHCO_3$ (equiv)	Temp (°C)	Time (h)	Yield[b] (%)
1	10	15:15	35	6	23
2	30	45:45	35	6	10[c]
3	50	75:75	35	6	<5[c]
4	20	30:30	55	3	38
5	5	7.5:7.5	55	3	34
6	10	15:15	55	3	35
7	10	15:15	60	2	41[d]

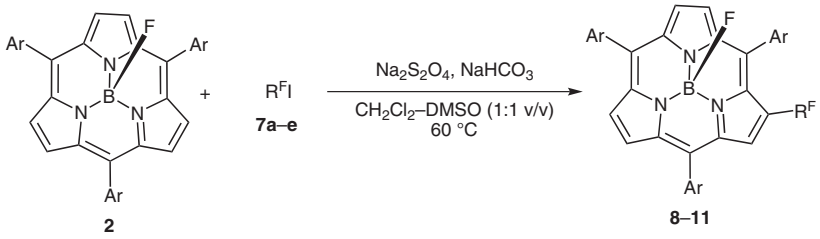
[a] Reaction conditions: subporphyrin **2a** (20 mg, 40.9 mmol), R^FI **7b**, $Na_2S_2O_4/NaHCO_3$, CH_2Cl_2–DMSO (1:1, 6 mL), N_2.
[b] Isolated yield.
[c] Polyperfluoroalkylated subporphyrins were generated.
[d] Conversion of substrate **2a** is 91%.

tures was beneficial to the reaction, and higher yield of the desired product was obtained even with a lower amount of initiator (entries 4–6). Finally, a combination of 10 equivalents of **7b** and 15 equivalents of sodium dithionite and sodium bicarbonate in dimethyl sulfoxide–dichloromethane (1:1) at 60 °C for two hours were the optimal conditions for the monoperfluoroalkylation of subporphyrins. Too much perfluoroalkyl iodide or sodium dithionite and sodium bicarbonate may be harmful and result in lower yields because of polyperfluoroalkylated byproducts are produced (entries 2 and 3).

As illustrated in Table 4, under the optimal conditions, a broad spectrum of subporphyrins and perfluoroalkyl iodides were examined. A variety of β-monoperfluoroalkylated subporphyrins were generated in acceptable yields.

With various β-mono(ω-chloroperfluorobutyl)subporphyrins in hand, their intramolecular cyclization and reductive defluorinative aromatization reactions were further investigated. Under the modified sulfinatodehalogenation conditions,[7c,9] the carbon–chloride bond of β-monoperfluoroalkylated subporphyrin was activated and the subsequent intramolecular cyclization reductive defluorinative aromatization reaction occurred successfully (Scheme 4). As expected, treatment of subporphyrin **11b** with 10 equivalents of sodium dithionite and sodium bicarbonate in dimethyl sulfoxide at 100 °C afforded β-monotetrafluorobenzo subporphyrin **15a** in good yield. In the case of subporphyrin **10a**, due to the shorter perfluoroalkyl chain, the corresponding subporphyrin β-perfluoroalkyl radical preferred to attack the *ortho*-carbon of the

Table 4 Synthesis of β-Perfluoroalkylated Subporphyrins



2 **8–11**

Entry	Substrate **2**	Ar	R^FI **7**	R^F	Product	Yield (%)
1	**2a**	Ph	**7a**	$(CF_2)_2Cl$	**8a**	31
2	**2a**	Ph	**7b**	$(CF_2)_4Cl$	**8b**	41
3	**2a**	Ph	**7c**	$(CF_2)_6Cl$	**8c**	34
4	**2b**	4-$F_3CC_6H_4$	**7b**	$(CF_2)_4Cl$	**9b**	46
5	**2c**	4-*t*-BuC_6H_4	**7a**	$(CF_2)_2Cl$	**10a**	35
6	**2c**	4-*t*-BuC_6H_4	**7b**	$(CF_2)_4Cl$	**10b**	40
7	**2d**	4-$MeOC_6H_4$	**7b**	$(CF_2)_4Cl$	**11b**	53
8	**2d**	4-$MeOC_6H_4$	**7c**	$(CF_2)_6Cl$	**11c**	35
9	**2d**	4-$MeOC_6H_4$	**7d**	$(CF_2)_4O(CF_2)_2SO_2F$	**11d**	42
10	**2d**	4-$MeOC_6H_4$	**7e**	$(CF_2)_8F$	**11e**	39

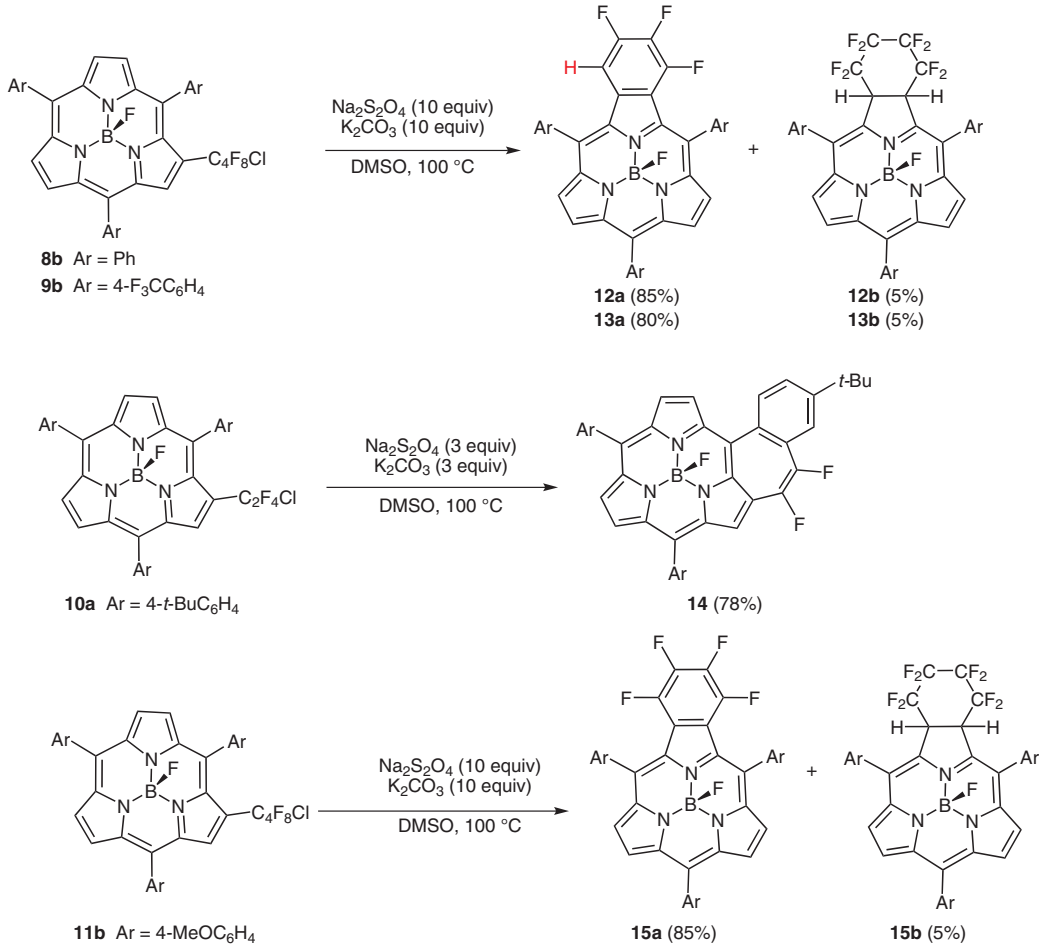
phenyl ring on the adjacent *meso*-position rather than the adjacent β-position. Subsequent reductive defluorinative aromatization produced the fluorinated seven-member-fused subporphyrin **14** in good yield. Interestingly, when subporphyrins **8b** and **9b** were utilized as the substrates, partial reduction products β-monotrifluorobenzo subporphyrin **12a** and **13a** were generated, respectively. In all these cases, intramolecular cyclization subchlorins were obtained as minor byproducts simultaneously.

A possible mechanism for the intramolecular cyclization reductive defluorinative aromatization reaction is illustrated in Scheme 5, which is similar to that of the corresponding porphyrins.[7c] However, the mechanism for the different products of the reactions according to the *meso*-aryl groups is not very clear and requires further study.

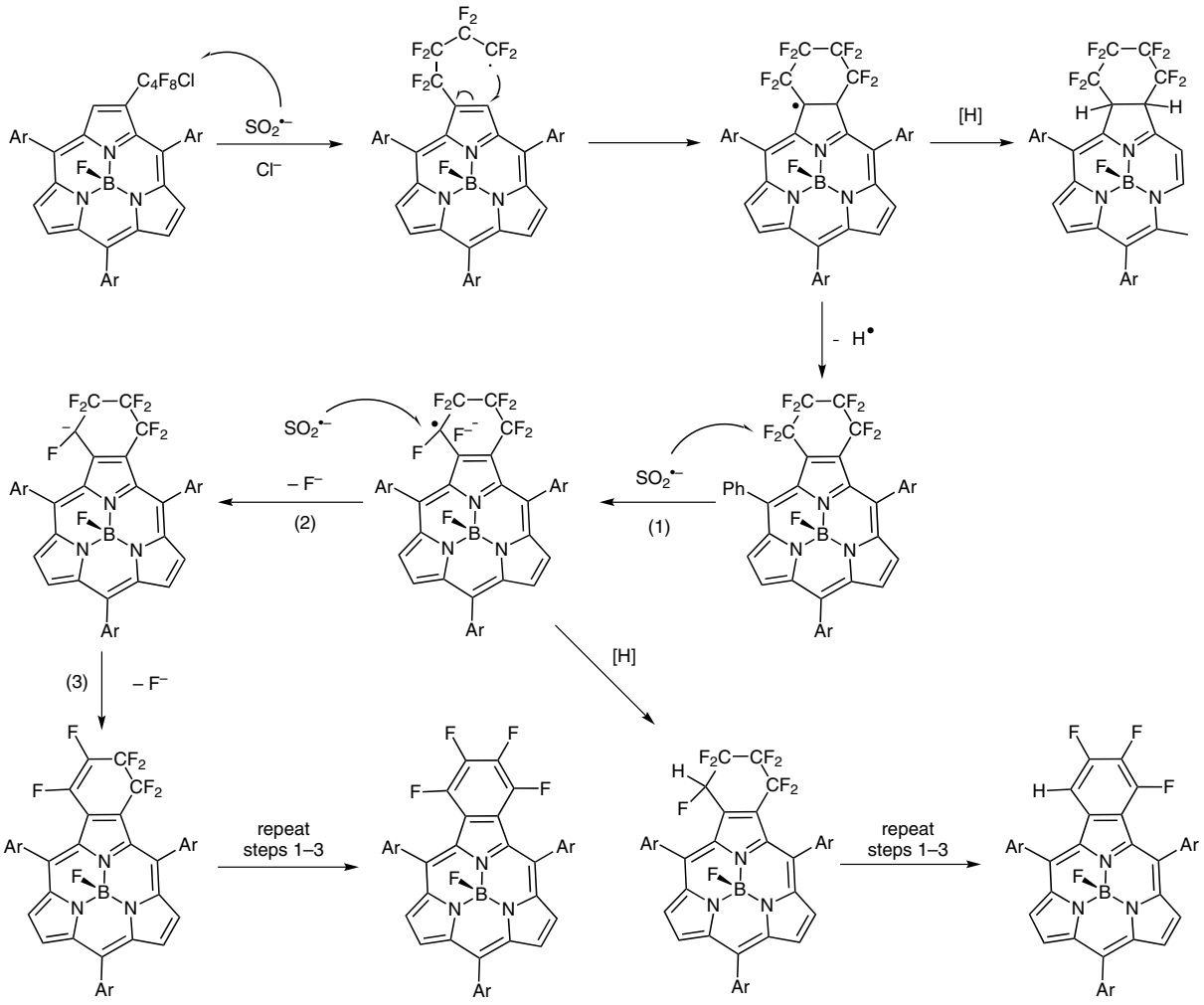
Figure 2 and Table 5 show the UV/Vis absorption and fluorescence emission spectra and data of typical perfluoroalkylated subporphyrins. Subporphyrin **2a** shows a Soret-like band at 368 nm and Q-like bands at 456 and 480 nm. β-Hexabromosubporphyrin **4a** shows a slightly more red-shifted Soret-like band at 370 nm which can be compared to that of **2a**, which demonstrated that macrocycle nonplanar distortion aroused by peripheral bromide substituents is not serious.[3g,10] When a trifluoromethyl group is introduced into the β-position, the absorption spectra of the corresponding subporphyrins are not influenced obviously. However, when six trifluoromethyl groups are installed into the periphery of subporphyrin, both the Soret-like band (396 nm) and the Q-like band (488, 518 nm) of β-hexakis(trifluoromethyl)subporphyrin **6a** are significantly red-shifted compared to those of **2a**, and the Soret-like band of subporphyrin **6a** has a shoulder-like peak at 377 nm. Moreover, the shape of the Q-like band is significantly altered from that of **2a**. Namely, the Q (0,0) bands are intensified and the Q (0,1) bands are weakened. All of these results might be attributed to severe macrocycle nonplanar distortion induced by trifluoromethyl groups and the electronic interaction of periphery substituents with *meso*-aryl groups.[3g,10]

As compared to subporphyrin **2a**, both Soret-like band and Q-like band of subporphyrin **12a** are obviously red-shifted, and the intensity of the Q-like band is greatly enhanced, which might originate from the effective π-conjugation with the fluorinated benzo group. These trends are similar to that of the corresponding porphyrins.[7c]

Along with these changes, the fluorescence spectra show the same trend, with peak positions of **2a**, **5a**, **8b**, **6a** at 510, 515, 517, and 540 nm, respectively. Influenced by peripheral hexakis(trifluoromethyl) substituents, fluorescence spectrum of **6a** is distinctly red-shifted. In contrast



Scheme 4 Intramolecular cyclization and reductive defluorinative aromatization reaction of various β-(chloroperfluoroalkyl)subporphyrins



Scheme 5 Proposed mechanism of intramolecular cyclization and reductive defluorinative aromatization reaction of β-mono(ω-chloroperfluorobutyl) subporphyrins

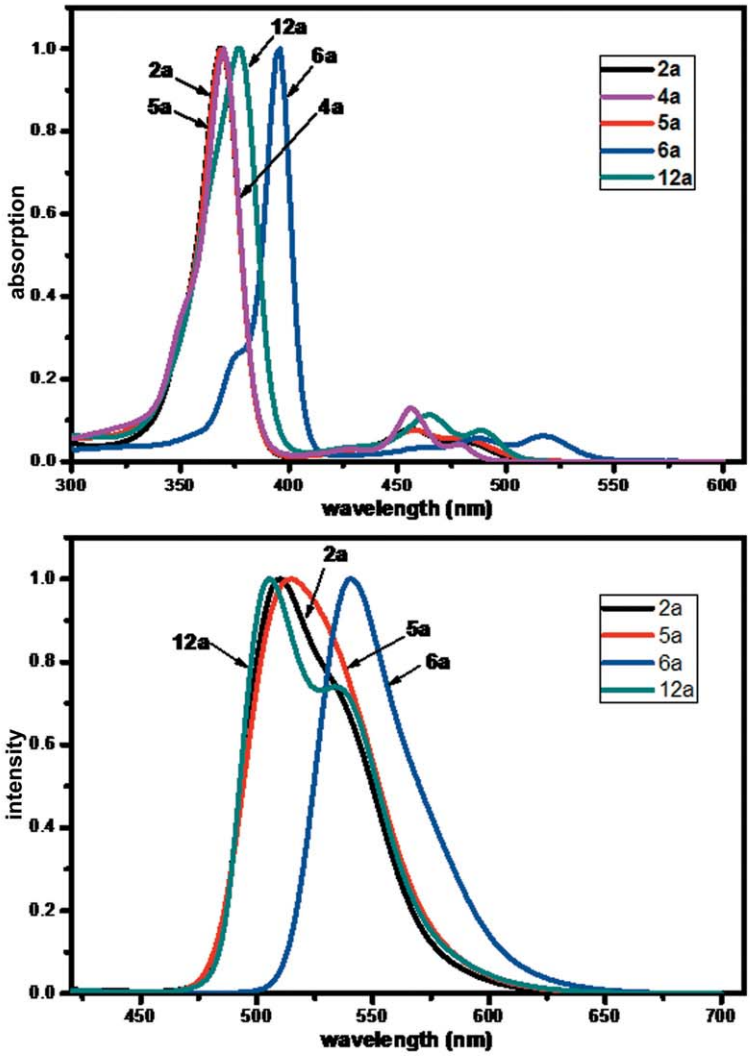
to the broad fluorescence spectra of **2a**, **5a**, and **6a**, subporphyrin **12a** exhibit a fluorescence spectrum of vibronic structure. This vibronic structure fluorescence may be ascribed to the benzo-structure and restricted *meso*-phenyl substituents.[3g]

Similar to porphyrins, the redox potentials of subporphyrins track their energy levels of HOMOs and LUMOs. Neglecting solvent effects, the differences between the first oxidation and reduction potential indicate the energy of the first absorption band of the subporphyrin, because this transition is principally a HOMO to LUMO excitation.[11,12] The oxidation and reduction potentials of substituted subporphyrins **5b**, **6b**, **9b**, **13a** were measured by cyclic voltammetry in dichloromethane containing 1×10^{-4} M tetrabutylammonium hexafluorophosphate as a supporting electrolyte in order to find out the influence of β-substituents on the electronic properties of subporphyrins. Subporphyrins **2b**, **5b**, and **6b** exhibited the first oxidation potential and reduction potential at 1.20 and –1.60 V, 1.35 and –1.36 V, and 2.11 and –0.55 V, respectively. These data show that the trifluoromethylated subporphyrins are more readily reduced and harder to oxidize with increasing substitution by trifluoromethyl groups. The observed electrochemical potential shift can be understood by the β-substituent effects, namely, the strong electron-withdrawing property of trifluoromethyl group could stabilize both LUMO and HOMO levels, thus reduce the first-reduction potential and enhance first-oxidation potential.[3g] As a sharp comparison, the first oxidation and reduction potentials of the corresponding porphyrin CuTPP and $CuTPP(CF_3)_8$ are 1.04 and –1.19 V and 0.99 and –0.39 V, respectively (Table 6). These data demonstrate that $CuTPP(CF_3)_8$ is both more readily reduced and oxidized than CuTPP. This trend can be explained as follows: both inductive effect and macrocycle distortion affect the level of HOMOs and LUMOs, and govern redox potentials. Electron-withdrawing substituents stabilize more the LUMOs than the HOMOs, while macrocycle distortion destabilizes the HOMOs and the LUMOs relatively unchanged.[12] In severely distorted porphyrins, the destabilizing effect on the HOMOs induce by macrocycle distortion predominates, which greatly elevate the HOMO level and lowers the first-oxidation potential.[7b] However,

steric congesting effects are not severe for subporphyrin aromatic macrocycles, and the electronic inductive effects of β-trifluoromethyl substituents take the dominant position for the electrochemical potentials.

With these oxidation and reduction potential data in hand, we can estimate the electrochemical HOMO–LUMO gaps of various subporphyrins. The HOMO–LUMO gaps of **2b**, **5b**, and **6b** are 2.80, 2.71, and 2.66 V, respectively. As a result, the red-shifted Q-like absorption bands for **5b** and **6b** were observed (Table 6).

A series of novel fluorinated subporphyrins have been efficiently synthesized by our trifluoromethylation reagent and modified sulfinatodehalogenation method for the first time. Various mono- and hexakistrifluoromethylated subporphyrins could be successfully generated with methyl 2,2-difluoro-2-(fluorosulfonyl)acetate and copper(I) iodide. A palladium catalyst is beneficial to the reaction, but not essential. Under modified sulfinatodehalogenation conditions, a variety of β-perfluoroalkylated subporphyrins were produced smoothly. The subsequent intramolecular cyclization reductive defluorinative aromatization of β-(ω-chloroperfluorobutyl)subporphyrins afforded valuable β-monotetrafluorobenzo and β-monotrifluorobenzo subporphyrins in good yield. The photophysical and electrochemical studies on several typical subporphyrins and porphyrins indicated the intensive influence of various perfluoroalkyl groups on the properties of subporphyrins.



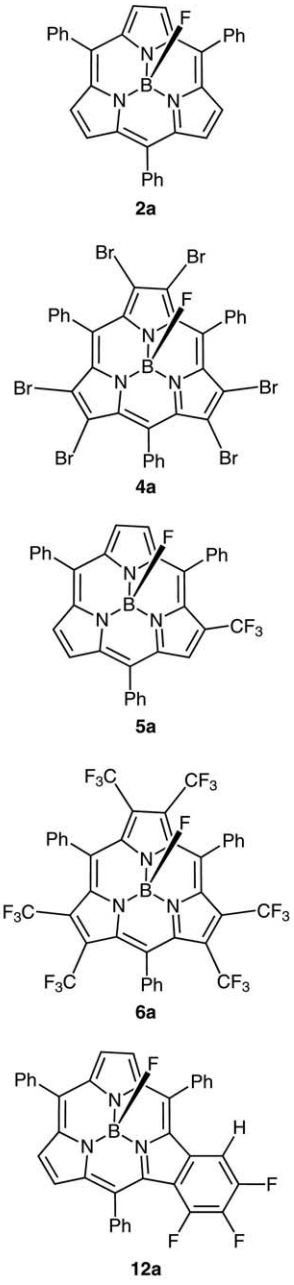


Figure 2 UV/Vis absorption and fluorescence emission spectra of **2a**, **4a**, **5a**, **6a**, **12a**

Table 5 UV/Vis Absorption and Fluorescence Emission Spectra Data for Various Subporphyrins (CH_2Cl_2, 25 °C)

Subporphyrins	Soret-like bands (nm)	Q-like bands (nm)	Fluorescence (nm)
2a	368	456, 480	510
4a	370	456, 478	–
5a	370	458, 476	515
6a	396 (377[a])	488, 518	540
8b	370	458, 480	517
12a	378	464, 488	505, 534
2b	368	456, 476	504
4b	368	456, 478	–
5b	368	456, 476	508
6b	390	482, 508	525
9b	370	458, 476	508
13a	376	466, 490	511
4c	374	458	–
6c	402	494, 525	537
2d	378	464, 494	546
5d	379	466, 494	557
11b	378	468, 496	549
15a	384	466, 488	537

[a] Shoulder absorption.

As the number of β-perfluoroalkyl substituents increasing, both Soret-like band and Q-like band of subporphyrins are significantly red-shifted due to macrocycle nonplanar distortion. β-Monotrifluorobenzo subporphyrins show a red-shifted Soret-like band and enhanced Q-like band caused mainly by extensive π-conjugation, which also exhibit a fluorescence spectrum of vibronic structure. The redox potentials of several typical subporphyrins were measured by cyclic voltammetry, and the HOMO–LUMO gap of β-hexakistrifluoromethylated subporphyrins illustrate that its macrocycle nonplanar distortion is not as serious as that of porphyrin, which can be supported by its ^{1}H NMR spectrum as well. Further studies on the synthesis of various fluorinated subporphyrin are now in progress in our laboratory.

NMR spectra were recorded at 400 MHz for ^{1}H and 376 MHz for ^{19}F NMR spectra. All spectra were obtained at r.t. in $CDCl_3$, except subporphyrins **4a**–**c** which were obtained at –40 °C; TMS was used as an internal standard ($\delta_{TMS} = 0$) for ^{1}H NMR spectra and $CFCl_3$ as an external standard (negative for upfield) for ^{19}F NMR spectra. Relative fluorescence quantum yields were determined with reference to that of 9,10-diphenylanthracene [$\Phi_F = 0.95$ (EtOH)]. Electrochemical properties of the compounds were investigated by cyclic voltammetry (CV) using a three-electrode cell with a glass carbon working electrode, a Pt wire counter electrode and an $Ag/AgNO_3$ reference electrode. Pure CH_2Cl_2 was used as solvent. The concentrations of the compounds were in the range of 10^{-6} M, and TBAF (10^{-4} M) was used as supporting electrolyte. Solution was purged with argon gas prior to measurements, and all measurement were made at 25 °C. TLC analysis was performed on silica gel plate and flash column chromatography over silica gel (300–400 mesh) (Huanghai Chemicals). DMSO and DMF were distilled from CaH_2. All the other solvents and chemicals were reagent grade, purchased commercially, and used without further purification if not noted.

***meso*-Triphenylsubporphyrin (2a); Typical Procedure**

To a solution of subporphyrin **1a** (49 mg, 0.1 mmol) in CH_2Cl_2 (10 mL), $BF_3{\cdot}OEt_2$ (0.25 mL, 2 mmol, 20 equiv) was added, and the resulting mixture was stirred at r.t. for 5 min; TLC indicated that the substrate was exhausted. The solvent was concentrated to dryness, the resulting residue was purified by column chromatography (silica gel, CH_2Cl_2–PE–Et_2O, 1:4:1) and recrystallization (CH_2Cl_2–MeOH) gave pure subporphyrin **2a** (45.6 mg, 95%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 6 H, β-H), 8.09 (d, 6 H, *o*-H_{Ph}), 7.73 (t, 6 H, *m*-H_{Ph}), 7.64 (t, 3 H, *p*-H_{Ph}).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –157.11 (m, 1 F, BF).

Table 6 Oxidation and Reduction Potentials of Subporphyrin **2b**, **5b**, **6b**, **9b**, and **13a** (CH_2Cl_2; V vs Ferrocene/Ferrocenium Ion Pair)[a]

Subporphyrin	Oxidation (V)	Reduction (V)			HOMO–LUMO Gap (V)	Q-like band λ_{max} (nm)
	$E^1_{1/2ox}$	$E^1_{1/2red}$	$E^2_{1/2red}$	$E^3_{1/2red}$		
2b	1.20	–1.60	–	–	2.80	476
5b	1.35	–1.36	–1.67	–	2.71	476
6b	2.11	–0.55	–1.10	–1.62	2.66	508
9b	1.44	–1.37	–1.85	—	2.81	476
13a	1.24	–1.45	–1.73	–2.09	2.69	490
CuTPP[b]	1.04	–1.19	–	–	2.23	647[b]
$CuTPP(CF_3)_8$[b]	0.99	–0.39	–	–	1.38	721[b]

[a] Measured by cyclic voltammetry, supporting electrolyte, Bu_4NPF_6 (10^{-4} M); working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, $Ag/AgNO_3$ (scan rate: 0.1 V/s).
[b] See ref.7c; TPP = *meso*-tetraphenylporphyrin, $TPP(CF_3)_8$ = β-octakis(trifluoromethyl)-*meso*-tetraphenylporphyrin.

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{33}H_{21}BN_3$: 469.1859; found: 469.1856.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 368 (20.6), 456 (1.6), 480 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 368 nm): λ_{max} = 510 nm.

***meso*-Tris[4-(trifluoromethyl)phenyl]subporphyrin (2b)**
From subporphyrin **1b**, chromatography (CH_2Cl_2–PE–Et_2O, 1:8:1), to give **2b** (64.8 mg, 97%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 6 H, β-H), 8.18 (d, 6 H, *o*-H_{Ph}), 8.00 (d, 6 H, *m*-H_{Ph}).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.41 (s, 9 F, CF_3), –157.20 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{36}H_{18}BN_3F_9$: 673.1481; found: 673.1482.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 368 (24), 456 (2.1), 476 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 368 nm): λ_{max} = 504 nm, Φ_F = 0.09.

***meso*-Tris(4-*tert*-butylphenyl)subporphyrin (2c)**
From subporphyrin **1c**, chromatography (CH_2Cl_2–PE–Et_2O, 1:8:1), to give **2c** (64 mg, 98%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 6 H, β-H), 8.03 (d, 6 H, *o*-H_{Ph}), 7.74 (d, 6 H, *m*-H_{Ph}), 1.52 (s, 27 H, *t*-Bu).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.85, 140.18, 134.10, 132.83, 125.73, 122.70, 120.60, 34.79, 31.50.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –157.09 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{45}H_{45}BN_3$: 637.3737; found: 637.3735.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 374 (13.4), 459 (1), 488 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 374 nm): λ_{max} = 518 nm.

***meso*-Tris(4-methoxyphenyl)subporphyrin (2d)**
From subporphyrin **1d**, chromatography (CH_2Cl_2–PE–EtOAc, 1:5:1), to give **2d** (54.5 mg, 94%) as an orange-reddish solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 6 H, β-H), 8.00 (d, 6 H, *o*-H_{Ph}), 7.26 (d, 6 H, *m*-H_{Ph}), 4.00 (s, 9 H, OMe).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –157.10 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{36}H_{27}BN_3O_3$: 559.2176; found: 559.2170.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 378 (13.1), 464 (1), 494 nm (1.42).

Fluorescence (CH_2Cl_2, λ_{ex} = 378 nm): λ_{max} = 546 nm, Φ_F = 0.12.

β-Monobromo-*meso*-triphenylsubporphyrin (3a); Typical Procedure
Compound **2a** (20 mg, 41 μmol) was dissolved in a mixture of DCE–MeOH (9:1, 8 mL), then NBS (8.0 mg, 45 μmol) was added, the resulting solution was heated to reflux and stirred for 2–3 h under N_2 atmosphere (monitored by TLC). The mixture was cooled to r.t., and then directly concentrated in vacuo; the residue was purified by column chromatography (silica gel, CH_2Cl_2–hexane–Et_2O, 1:5:1) to give **3a** (21 mg, 91%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17–8.23 (m, 5 H, β-H), 8.05–8.10 (m, 4 H, *o*-H_{Ph}), 7.91 (br s, 2 H, *o*-H_{Ph}), 7.66–7.76 (m, 9 H, *m*,*p*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.98, 141.81, 141.42, 141.33, 139.92, 137.59, 137.41, 136.79, 135.74, 134.11, 134.04, 129.75, 129.34, 129.17, 129.10, 128.83, 125.50, 124.30, 124.13, 123.75, 123.61, 122.25, 121.97, 121.34, 113.51.

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{33}H_{20}BN_3Br$: 547.0946; found: 547.0965.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 370 (11.7), 456 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 370 nm): λ_{max} = 511 nm, Φ_F = 0.03.

β-Monobromo-*meso*-tris[4-(trifluoromethyl)phenyl]subporphyrin (3b)
From subporphyrin **2b**, chromatography (CH_2Cl_2–PE–Et_2O, 1:10:1), to give **3b** (28 mg, 89%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.21 (m, 5 H, β-H), 8.15–8.17 (m, 4 H, *o*-H_{Ph}), 7.95–8.02 (m, 8 H, *o*,*m*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.18, 140.96, 140.59, 140.57, 139.92, 139.77, 139.13, 138.22, 135.80, 133.22, 133.17, 131.01, 130.69, 130.40, 130.34, 125.82, 125.79, 125.63, 125.55, 124.89, 124.86, 124.48, 123.51, 123.35, 123.02, 122.83, 119.99, 119.87, 119.09, 113.08.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.31 (s, 3 F, CF_3), –62.40 (s, 3 F, CF_3), –62.44 (s, 3 F, CF_3), –157.2 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{36}H_{17}BN_3F_9Br$: 751.0606; found: 751.0586.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 368 (10.6), 456 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 368 nm): λ_{max} = 508, 529 nm, Φ_F = 0.03.

β-Monobromo-*meso*-tris(4-methoxyphenyl)subporphyrin (3d)
From subporphyrin **2d**, chromatography (PE–EtOAc, 2:1), to give **3d** (25.6 mg, 95%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 5.6 Hz, 4 H, β-H), 8.11 (s, 1 H, β-H), 7.95–8.00 (m, 4 H, *o*-H_{Ph}), 7.79 (br s, 2 H, *o*-H_{Ph}), 7.19–7.28 (m, 6 H, *m*-H_{Ph}), 4.01 (s, 6 H, OMe), 4.00 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.87, 159.78, 140.65, 140.50, 140.03, 138.67, 135.92, 134.34, 134.01, 133.95, 128.98, 128.78, 126.98, 124.29, 122.97, 122.77, 122.40, 122.30, 120.82, 120.32, 120.03, 119.83, 114.31, 113.37, 113.28, 112.22.

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{36}H_{26}BN_3O_3Br$: 637.1281; found: 637.1281.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 378 (12), 462 (1), 490 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 378 nm): λ_{max} = 539 nm, Φ_F = 0.004.

β-Hexabromo-*meso*-triphenylsubporphyrin (4a)
From subporphyrin **2a** (25 mg, 50 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:4:1), to give **4a** (45.7 mg, 95%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, –40 °C): δ = 8.12 (d, *J* = 7.80 Hz, 3 H, *o*-H_{Ph}), 7.75 (t, *J* = 7.80 Hz, 3 H, *m*-H_{Ph}), 7.70 (t, *J* = 7.80 Hz, 3 H, *p*-H_{Ph}), 7.51 (t, *J* = 7.80 Hz, 3 H, *m*-H_{Ph}), 7.25 (d, *J* = 7.80 Hz, 3 H, *o*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.38, 133.08, 132.50, 131.86, 129.34, 127.65, 120.14, 118.42.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –157.17 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{33}H_{15}BN_3Br_6$: 936.6490; found: 936.6522.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 370 (23), 456 (3), 478 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 370 nm): λ_{max} = 518 nm, Φ_F = 0.002.

β-Hexabromo-*meso*-tris[4-(trifluoromethyl)phenyl]subporphyrin (4b)
From subporphyrin **2b** (30 mg, 43 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:20:1), to give **4b** (41 mg, 82%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, –40 °C): δ = 8.28 (d, *J* = 7.80 Hz, 3 H, *o*-H_{Ph}), 8.04 (d, *J* = 7.80 Hz, 3 H, *m*-H_{Ph}), 7.78 (d, *J* = 7.80 Hz, 3 H, *m*-H_{Ph}), 7.41 (d, *J* = 7.80 Hz, 3 H, *o*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.51, 134.44, 133.48, 132.87, 132.44, 132.11, 131.79, 131.46, 128.22, 125.50, 125.10, 124.53, 122.79, 120.08, 118.75, 118.65.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.30 (s, 9 F, CF_3), –156.83 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{36}H_{12}BN_3F_9Br_6$: 1140.6190; found: 1140.6163.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 468 (17.5), 456 (2.2), 478 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 368 nm): λ_{max} = 517, 486 nm, Φ_F = 0.002.

β-Hexabromo-*meso*-tris(4-*tert*-butylphenyl)subporphyrin (4c)
From subporphyrin **2c** (70 mg, 106 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:8:1), to give **4c** (120 mg, 100%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, –40 °C): δ = 8.02 (d, *J* = 7.80 Hz, 3 H, *o*-H_{Ph}), 7.74 (d, *J* = 7.80 Hz, 3 H, *m*-H_{Ph}), 7.49 (d, *J* = 7.80 Hz, 3 H, *m*-H_{Ph}), 7.16 (d, *J* = 7.80 Hz, 3 H, *o*-H_{Ph}), 1.48 (s, 27 H, *t*-Bu).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.74, 134.44, 132.38, 130.86, 128.74, 124.55, 120.32, 118.32, 34.91, 31.59.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –157.10 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{45}H_{39}BN_3Br_6$: 1104.8368; found: 1104.8399.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 374 (26), 458 nm (3.75).

Fluorescence (in CH_2Cl_2, λ_{ex} = 374 nm): λ_{max} = 521 nm, Φ_F = 0.001.

β-Mono(trifluoromethyl)-*meso*-triphenylsubporphyrin (5a); Typical Procedure
Under an N_2 atmosphere, $FSO_2CF_2CO_2Me$ (135 mg, 0.7 mmol) was added to a mixture of **3a** (20 mg, 35.2 μmol), $Pd(dba)_2$ (5 mol%), and CuI (130 mg, 0.7 mmol) in anhyd DMF (4 mL), the resulting mixture was stirred at 100 °C under N_2 for 2 h. The mixture was cooled to r.t. and then it was diluted with CH_2Cl_2 (10 mL) and passed through a short column (silica gel). The filtrate was washed with H_2O (3×), dried (anhyd Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2–hexane–Et_2O, 1:10:1) to give **5a** (17.8 mg, 94%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1 H, β-H), 8.26 (d, *J* = 4.4 Hz, 1 H, β-H), 8.22 (d, *J* = 4.8 Hz, 1 H, β-H), 8.20 (d, *J* = 4.8 Hz, 1 H, β-H), 8.16 (d, *J* = 4.8 Hz, 1 H, β-H), 8.05–8.08 (m, 4 H, *o*-H_{Ph}), 7.66–7.77 (m, 11 H, *o*,*m*,*p*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.74, 141.51, 141.15, 140.25, 136.34, 136.28, 136.08, 135.55, 134.62, 133.14, 133.12, 128.95, 128.89, 128.49, 128.47, 128.25, 127.70, 127.44, 125.36, 124.99, 124.52, 124.02, 123.71, 123.62, 123.54, 123.49, 123.14, 122.70, 121.62, 121.21, 120.86.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –53.67 (s, 3 F, β-CF_3), –157.77 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{34}H_{20}BN_3F_3$: 537.1715; found: 537.1733.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 370 (17.5), 458 (1.3), 476 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 370 nm): λ_{max} = 515 nm, Φ_F = 0.09.

β-Mono(trifluoromethyl)-*meso*-tris[4-(trifluoromethyl)phenyl]subporphyrin (5b)
From subporphyrin **3b** (13 mg, 16.8 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:15:1) to give **5b** (11 mg, 86%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H, β-H), 8.25 (d, *J* = 4.8 Hz, 1 H, β-H), 8.22 (d, *J* = 4.8 Hz, 1 H, β-H), 8.13–8.20 (m, 2 H, β-H, 4 H, *o*-H_{Ph}), 7.91–8.03 (m, 6 H, *m*-H_{Ph}); *o*-H_{Ph} (2 H, undetected).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.84, 141.66, 141.37, 140.48, 139.62, 139.35, 138.88, 136.36, 134.45, 133.23, 133.20, 131.11, 131.03, 130.78, 125.92, 125.58, 125.50, 124.51124.26, 123.93, 123.79, 123.33, 121.41, 119.90, 119.74.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –53.60 (s, 3 F, β-CF_3), –62.43 (s, 3 F, CF_3), –62.44 (s, 3 F, CF_3), –62.48 (s, 3 F, CF_3), –157.76 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{37}H_{17}BN_3F_{12}$: 741.1340; found: 741.1355.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 368 (19), 456 (1.6), 476 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 368 nm): λ_{max} = 508 nm, Φ_F = 0.08.

β-Mono(trifluoromethyl)-*meso*-tris(4-methoxyphenyl)subporphyrin (5d)
From subporphyrin **3d** (13 mg, 19.7 μmol), chromatography (PE–EtOAc, 4:1), to give **5d** (12 mg, 95%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H, β-H), 8.25 (d, *J* = 4.8 Hz, 1 H, β-H), 8.21 (d, *J* = 4.8 Hz, 1 H, β-H), 8.19 (d, *J* = 4.8 Hz, 1 H, β-H), 8.15 (d, *J* = 4.8 Hz, 1 H, β-H), 7.98–8.01 (m, 4 H, *o*-H_{Ph}), 7.79 (br s, 2 H, *o*-H_{Ph}), 7.26–7.30 (m, 4 H, *m*-H_{Ph}), 7.18 (d, *J* = 8 Hz, 2 H, *m*-H_{Ph}), 4.02 (s, 9 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.14, 159.94, 141.60, 141.26, 140.82, 139.95, 136.16, 134.93, 134.18, 134.13, 128.81, 128.53, 128.00, 125.17, 124.80, 124.42, 124.13, 123.73, 123.44, 123.37, 122.93, 122.33, 121.74, 120.92, 120.29, 114.58, 114.51, 112.97, 55.54, 55.24.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –53.57 (s, 3 F, β-CF_3), –157.60 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{37}H_{26}BN_3O_3F_3$: 627.2063; found: 627.2050.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 379 (12.3), 466 (1), 494 nm (1.2).

Fluorescence (CH_2Cl_2, λ_{ex} = 378 nm): λ_{max} = 557 nm, Φ_F = 0.12.

β-Hexakis(trifluoromethyl)-*meso*-triphenylsubporphyrin (6a); Typical Procedure
Under an N_2 atmosphere, $FSO_2CF_2CO_2Me$ (237 mg, 1.23 mmol) was added to a mixture of **4a** (40 mg, 41 μmol), $Pd(dba)_2$ (5 mol%) and CuI (234 mg, 1.23 mmol) in anhyd DMF (8 mL), the resulting mixture was stirred at 100 °C under N_2 for 2 h. The mixture was cooled to r.t., and then it was diluted with CH_2Cl_2 (30 mL) and passed through a short column (silica gel). The filtrate was washed with H_2O (3 ×), dried (anhyd Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2–hexane–Et_2O, 1:15:1) to give **6a** (33 mg, 90%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 6.8 Hz, 6 H, *o*-H_{Ph}), 7.72 (t, *J* = 7.6 Hz, 3 H, *p*-H_{Ph}), 7.62 (t, *J* = 8.0 Hz, 6 H, *m*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.10, 133.32, 129.98, 127.28, 125.75, 122.25, 119.52.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –50.25 (s, 18 F, β-CF_3), –158.3 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{39}H_{15}BN_3F_{18}$: 877.1088; found: 877.1102.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 396 (17.5), 488 (1), 518 nm (1.1).

Fluorescence (CH_2Cl_2, λ_{ex} = 396 nm): λ_{max} = 540 nm, Φ_F = 0.02.

β-Hexakis(trifluoromethyl)-*meso*-tris[4-(trifluoromethyl)phenyl]subporphyrin (6b)
From subporphyrin **4b** (35 mg, 30 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:20:1), to give **6b** (28 mg, 85%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 12 H, *o*,*m*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.96, 135.81, 135.24, 134.41, 134.08, 133.76, 133.55, 126.97, 126.13, 126.09, 126.06, 124.25, 123.70, 120.97.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –49.99 (s, 18 F, β-CF_3), –62.67 (s, 9 F, CF_3), –157.95 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{42}H_{12}BN_3F_{27}$: 1081.0690; found: 1081.0724.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 390 (24), 482 (1.5), 508 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 390 nm): λ_{max} = 525 nm, Φ_F = 0.01.

β-Hexakis(trifluoromethyl)-*meso*-tris(4-*tert*-butylphenyl)subporphyrin (6c)
From subporphyrin **4c** (30 mg, 27 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:50:1), to give **6c** (25 mg, 87%) as an orange-reddish solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8 Hz, 6 H, *o*-H_{Ph}), 7.61 (d, *J* = 8 Hz, 6 H, *m*-H_{Ph}), 1.49 (s, 27 H, *t*-Bu).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.33, 137.06, 134.07, 131.44, 130.26, 130.07, 129.90, 129.84, 129.69, 128.31, 128.22, 128.13, 126.67, 123.33, 121.16, 120.68, 118.51, 118.02, 115.85, 66.47, 66.40, 54.54, 45.32, 28.38, 25.98, 18.07, 18.02.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –50.37 (s, 18 F, β-CF_3), –158.3 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{51}H_{39}BN_3F_{18}$: 1045.3024; found: 1045.2980.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 402 (13), 494 (1), 525 nm (1.5).

Fluorescence (CH_2Cl_2, λ_{ex} = 402 nm): λ_{max} = 537 nm, Φ_F = 0.02.

β-Mono(perfluoroalkyl)-*meso*-triarylsubporphyrins; General Procedure
Using **2a** as model substrate, **2a** (20 mg, 40.9 μmol) was dissolved in a mixture of CH_2Cl_2–DMSO (1:1, 6 mL), then R^FI (0.41 mmol), $Na_2S_2O_4$ (0.62 mmol), and $NaHCO_3$ (0.62 mmol) were added, the resulting solution was heated to reflux and stirred for 2–3 h under an N_2 atmosphere (monitored by TLC). The mixture was cooled to r.t., then it was diluted with CH_2Cl_2 (10 mL) and passed through a short column (silica gel). The filtrate was washed H_2O (3 ×), dried (anhyd Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2–hexane–Et_2O, 1:15:1) to give the product.

Subporphyrin 8a
From subporphyrin **2a** (30 mg, 61 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:15:1), to give **8a** (12 mg, 31%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1 H, β-H), 8.24 (d, *J* = 4.8 Hz, 1 H, β-H), 8.22 (d, *J* = 4.8 Hz, 1 H, β-H), 8.17 (d, *J* = 4.8 Hz, 1 H, β-H), 8.04–8.07 (m, 5 H, β-H, *o*-H_{Ph}), 7.63–7.77 (m, 9 H, *m*,*p*-H_{Ph}), 7.57 (br s, 1 H, *o*-H_{Ph}), 7.41 (br s, 1 H, *o*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.57, 141.74, 141.29, 140.41, 136.52, 136.31, 135.66, 134.13, 133.33, 132.04, 129.14, 129.11, 128.70, 128.46, 127.19, 125.44, 124.73, 124.06, 123.91, 123.51, 123.19, 122.78, 121.32, 121.20.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –67.13 (d, 2 F, CF_2Cl), –96.09 (t, 2 F, SubPor-CF_2), –158.01 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{35}H_{20}BN_3F_4Cl$: 603.1406; found: 603.1415.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 370 (16), 458 (1.1), 480 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 370 nm): λ_{max} = 517 nm, Φ_F = 0.11.

Subporphyrin 8b
From subporphyrin **2a** (15 mg, 30 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:15:1), to give **8b** (8.8 mg, 41%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, β-H), 8.25 (d, *J* = 4.8 Hz, 1 H, β-H), 8.23 (d, *J* = 4.8 Hz, 1 H, β-H), 8.17 (d, *J* = 4.8 Hz, 1 H, β-H), 8.05–8.07 (m, 5 H, β-H, *o*-H_{Ph}), 7.63–7.78 (m, 9 H, *m*,*p*-H_{Ph}), 7.54 (br s, 1 H, *o*-H_{Ph}), 7.40 (br s, 1 H, *o*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.33, 141.53, 141.08, 140.07, 136.29, 136.15, 136.05, 135.37, 133.87, 133.16, 133.09, 131.67, 128.96, 128.88, 128.49, 128.22, 128.17, 126.98, 125.47, 124.54, 123.88, 123.7, 123.52, 123.23, 122.99, 122.61, 122.41, 122.06, 121.08, 120.96, 116.34, 116.01, 115.67, 109.67.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –68.01 (t, *J* = 15 Hz, 2 F, CF_2Cl), –98.35 (m, 2 F, SubPor-CF_2), –117.41 (m, 2 F, CF_2CF_2Cl), –119.68 (t, *J* = 15 Hz, 2 F, SubPor-CF_2CF_2), –158.12 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{37}H_{20}BN_3F_8Cl$: 703.1356; found: 703.1342.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 370 (16), 458 (1.2), 480 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 370 nm): λ_{max} = 517 nm, Φ_F = 0.10.

Subporphyrin 8c
From subporphyrin **2a** (40 mg, 82 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:15:1), to give **8c** (24 mg, 34%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, β-H), 8.25 (d, *J* = 4.8 Hz, 1 H, β-H), 8.23 (d, *J* = 4.8 Hz, 1 H, β-H), 8.17 (d, *J* = 4.8 Hz, 1 H, β-H), 8.05–8.07 (m, 5 H, β-H, *o*-H_{Ph}), 7.63–7.78 (m, 9 H, *m*,*p*-H_{Ph}), 7.54 (br s, 1 H, *o*-H_{Ph}), 7.40 (br s, 1 H, *o*-H_{Ph}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.33, 141.54, 141.09, 140.08, 136.29, 136.24, 136.05, 135.35, 133.84, 133.15, 133.09, 131.64, 129.14, 128.96, 128.88, 128.50, 128.22, 128.19, 126.97, 125.49, 124.79, 124.54, 123.89, 123.73, 123.47, 123.18, 122.99, 122.62, 121.79, 121.08, 120.95, 116.09, 113.22.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –67.95 (m, 2 F, CF_2Cl), –98.37 (m, 2 F, SubPor-CF_2), –117.41 to –121.82 (m, 8 F), –158.12 (m, 1 F, BF).

HR-MALDI TOF-MS: *m*/*z* [M – F]$^+$ calcd for $C_{39}H_{20}BN_3F_{12}Cl$: 803.1276; found: 803.1278.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 370 (16), 458 (1.2), 480 nm (1).

Fluorescence (in CH_2Cl_2, λ_{ex} = 370 nm): λ_{max} = 517 nm, Φ_F = 0.09.

Subporphyrin 9b
From subporphyrin **2b** (25 mg, 34.5 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:15:1), to give **9b** (12 mg, 46%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 1 H, β-H), 8.43 (s, 1 H, β-H), 8.30 (s, 1 H, β-H), 8.26 (d, *J* = 4.8 Hz, 1 H, β-H), 8.24 (d, *J* = 4.8 Hz, 1 H, β-H), 8.16–8.19 (m, 4 H, *o*-H_{Ph}), 8.01–8.08 (m, 6 H, *m*-H_{Ph}), 7.84 (br s, 2 H, *o*-H_{Ph}).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.48 (s, 3 F, CF_3), –62.51 (s, 3 F, CF_3), –62.62 (s, 3 F, CF_3), –68.18 (m, 2 F, CF_2Cl), –98.33 (m, 2

F, SubPor-CF_2), –117.55 (m, 2 F, CF_2CF_2Cl), –119.88 (t, J = 15 Hz, 2 F, SubPor-CF_2CF_2), –158.07 (m, 1 F, BF).

HRMS (MALDI TOF): m/z $[M - F]^+$ calcd for $C_{40}H_{17}BN_3F_{17}Cl$: 907.0963; found: 907.0963.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 370 (15), 458 (1.4), 476 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 370 nm): λ_{max} = 508 nm, Φ_F = 0.12.

Subporphyrin 10a

From subporphyrin **2c** (40 mg, 60.8 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:20:1), to give **10a** (16.8 mg, 35%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1 H, β-H), 8.24 (d, J = 4.8 Hz, 1 H, β-H), 8.23 (d, J = 4.8 Hz, 1 H, β-H), 8.19 (d, J = 4.8 Hz, 1 H, β-H), 8.10 (d, J = 4.8 Hz, 1 H, β-H), 7.99 (m, 4 H, o-H_{Ph}), 7.76 (t, J = 7.6 Hz, 4 H, m-H_{Ph}), 7.60 (br s, 1 H, o-H_{Ph}, 2 H, m-H_{Ph}), 7.36 (br s, 1 H, o-H_{Ph}), 1.52 (s, 9 H, t-Bu), 1.51 (s, 9 H, t-Bu), 1.50 (s, 9 H, t-Bu).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.69, 151.40, 151.34, 142.36, 141.57, 141.06, 140.23, 136.28, 135.77, 133.71, 133.47, 133.07, 132.99, 126.21, 126.10, 125.53, 124.60, 124.01, 123.84, 123.10, 122.67, 121.21, 35.06, 35.02, 34.99, 31.69, 31.68.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –66.78 (m, 2 F, CF_2Cl), –95.96 (m, 2 F, SubPor-CF_2), –157.96 (m, 1 F, BF).

HRMS (MALDI TOF): m/z $[M - F]^+$ calcd for $C_{47}H_{44}BN_3F_4Cl$: 771.3284; found: 771.3299.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 374 (13.5), 462 (1), 488 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 374 nm): λ_{max} = 527 nm, Φ_F = 0.09.

Subporphyrin 10b

From subporphyrin **2c** (40 mg, 60.8 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:20:1), to give **10b** (21.6 mg, 40%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1 H, β-H), 8.27 (d, J = 4.8 Hz, 1 H, β-H), 8.24 (d, J = 4.8 Hz, 1 H, β-H), 8.20 (d, J = 4.8 Hz, 1 H, β-H), 8.11 (d, J = 4.8 Hz, 1 H, β-H), 8.00 (m, 4 H, o-H_{Ph}), 7.76 (t, J = 7.6 Hz, 4 H, m-H_{Ph}), 7.60 (br s, 1 H, o-H_{Ph}, 2 H, m-H_{Ph}), 7.35 (br s, 1 H, o-H_{Ph}), 1.53 (s, 9 H, t-Bu), 1.52 (s, 9 H, t-Bu), 1.50 (s, 9 H, t-Bu).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.49, 151.19, 151.05, 142.18, 141.38, 140.89, 139.91, 136.09, 135.55, 133.48, 133.23, 133.14, 132.87, 132.79, 126.00, 125.90, 125.58, 124.42, 123.86, 123.65, 123.36, 123.07, 122.90, 122.54, 122.09, 120.99, 116.12, 34.85, 34.81, 34.74, 31.92, 31.46, 31.42, 29.36, 22.69, 14.12.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –67.99 (t, J = 12 Hz, 2 F, CF_2Cl), –98.15 (m, 2 F, SubPor-CF_2), –117.21 (m, 2 F, CF_2), –119.82 (t, J = 15 Hz, 2 F, CF_2), –158.00 (m, 1 F, BF).

HRMS (MALDI TOF): m/z $[M - F]^+$ calcd for $C_{49}H_{44}BN_3F_8Cl$: 871.3220; found: 871.3223.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 374 (13.5), 462 (1), 488 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 374 nm): λ_{max} = 527 nm, Φ_F = 0.10.

Subporphyrin 11b

From subporphyrin **2d** (40 mg, 69 μmol), chromatography (PE–EtOAc (4:1), to give **11b** (29.7 mg, 53%) as an orange-reddish solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H, β-H), 8.22 (d, J = 4.8 Hz, 1 H, β-H), 8.20 (d, J = 4.8 Hz, 1 H, β-H), 8.14 (d, J = 4.8 Hz, 1 H, β-H), 8.05 (d, J = 4.8 Hz, 1 H, β-H), 7.97–8.00 (m, 4 H, o-H_{Ph}), 7.26–7.30 (m, 6 H, m-H_{Ph}), 7.13 (br s, 2 H, o-H_{Ph}), 4.02 (s, 3 H, OMe), 4.01 (s, 3 H, OMe), 3.99 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.12, 159.91, 159.71, 142.26, 141.28, 140.72, 139.78, 136.10, 135.71, 134.91, 134.21, 134.11, 132.82, 128.75, 128.58, 128.48, 125.39, 124.25, 123.63, 123.49, 123.25, 122.97, 122.81, 122.42, 122.29, 120.80, 120.31, 116.07, 114.60, 114.50, 112.42, 55.52.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –67.99 (t, J = 15 Hz, 2 F, CF_2Cl), –98.10 (m, 2 F, SubPor-CF_2), –117.45 (m, 2 F, CF_2CF_2Cl), –119.63 (t, J = 15 Hz, 2 F, SubPor-CF_2CF_2), –157.98 (m, 1 F, BF).

HRMS (MALDI TOF): m/z $[M - F]^+$ calcd for $C_{40}H_{26}BN_3O_3F_8Cl$: 793.1659; found: 793.1669.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 378 (11), 468 (1), 496 nm (1.3).

Fluorescence (CH_2Cl_2, λ_{ex} = 378 nm): λ_{max} = 549 nm, Φ_F = 0.12.

Subporphyrin 11c

From subporphyrin **2d** (30 mg, 51.8 μmol), chromatography (PE–EtOAc, 4:1), to give **11c** (16.5 mg, 35%) as an orange-reddish solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1 H, β-H), 8.21 (d, J = 4.8 Hz, 1 H, β-H), 8.18 (d, J = 4.8 Hz, 1 H, β-H), 8.13 (d, J = 4.8 Hz, 1 H, β-H), 8.04 (d, J = 4.8 Hz, 1 H, β-H), 7.97 (m, 4 H, o-H_{Ph}), 7.27 (m, 6 H, m-H_{Ph}), 7.11 (br s, 2 H, o-H_{Ph}), 4.01 (s, 3 H, OMe), 4.00 (s, 3 H, OMe), 3.97 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.14, 159.92, 159.75, 142.27, 141.30, 140.74, 139.79, 136.08, 135.70, 134.20, 134.10, 128.75, 128.48, 125.39, 124.25, 123.63, 123.49, 122.81, 122.30, 120.80, 120.30, 114.60, 114.49, 112.40, 55.52, 55.45.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –67.96 (t, J = 15 Hz, 2 F, CF_2Cl), –98.10 (m, 2 F, SubPor-CF_2), –117.97 to –121.83 (m, 8 F), –157.98 (m, 1 F, BF).

HRMS (MALDI TOF): m/z $[M - F]^+$ calcd for $C_{42}H_{26}BN_3O_3F_{12}Cl$: 893.1595; found: 893.1605.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 380 (13), 466 (1), 496 nm (1.3).

Fluorescence (CH_2Cl_2, λ_{ex} = 380 nm): λ_{max} = 549 nm, Φ_F = 0.11.

Subporphyrin 11d

From subporphyrin **2d** (25 mg, 43 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:5:1), to give **11d** (17.6 mg, 42%) as an orange-reddish solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, β-H), 8.23 (d, J = 4.8 Hz, 1 H, β-H), 8.20 (d, J = 4.8 Hz, 1 H, β-H), 8.14 (d, J = 4.8 Hz, 1 H, β-H), 8.05 (d, J = 4.8 Hz, 1 H, β-H), 7.98 (m, 4 H, o-H_{Ph}), 7.28 (t, J = 8.8 Hz, 6 H, m-H_{Ph}), 7.12 (br s, 2 H, o-H_{Ph}), 4.02 (s, 3 H, OMe), 4.01 (s, 3 H, OMe), 3.99 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.15, 159.93, 159.76, 142.28, 141.33, 140.77, 139.81, 136.02, 135.64, 134.80, 134.20, 134.10, 132.89, 128.72, 128.46, 125.34, 124.28, 123.67, 123.52, 123.16, 122.85, 122.59, 122.34, 120.82, 120.27, 114.60, 114.50, 113.25, 112.46, 112.09, 55.52, 55.44.

^{19}F NMR (376 MHz, $CDCl_3$): δ = 45.89 (s, 1 F, SO_2F), –81.88 (s, 2 F, CF_2O), –82.97 (s, 2 F, CF_2O), –98.15 (m, 2 F, SubPor-CF_2), –118.53 (m, 4 F, CF_2), –125.00 (t, J = 15 Hz, 2 F, SubPor-CF_2CF_2), –157.80 (m, 1 F, BF).

HRMS (MALDI TOF): m/z $[M - F]^+$ calcd for $C_{42}H_{26}BN_3O_6F_{13}S$: 957.1459; found: 957.1448.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 380 (13), 466 (1), 496 nm (1.3).

Fluorescence (CH_2Cl_2, λ_{ex} = 380 nm): λ_{max} = 549 nm, Φ_F = 0.13.

Subporphyrin 11e

From subporphyrin **2d** (25 mg, 43 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:5:1), to give **11e** (16 mg, 39%) as an orange-reddish solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, β-H), 8.23 (d, *J* = 4.8 Hz, 1 H, β-H), 8.20 (d, *J* = 4.8 Hz, 1 H, β-H), 8.15 (d, *J* = 4.8 Hz, 1 H, β-H), 8.05 (d, *J* = 4.8 Hz, 1 H, β-H), 7.98 (m, 4 H, *o*-H_{Ph}), 7.28 (t, *J* = 8.8 Hz, 6 H, *m*-H_{Ph}), 7.12 (br s, 2 H, *o*-H_{Ph}), 4.02 (s, 3 H, OMe), 4.01 (s, 3 H, OMe), 3.98 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.14, 159.93, 159.76, 142.28, 141.31, 140.75, 139.79, 136.07, 135.68, 134.88, 134.20, 134.10, 132.71, 128.74, 128.47, 125.40, 124.26, 123.64, 123.50, 123.13, 122.82, 122.32, 120.81, 120.29, 118.53, 116.58, 116.15, 114.93, 114.60, 114.50, 113.58, 112.51, 111.03, 110.77, 108.16, 55.52, 55.41.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.75 (d, *J* = 9.8 Hz, 3 F, CF_3), –98.16 (m, 2 F, SubPor-CF_2), –118.15 (m, 2 F), –121.51 (s, 2 F), –121.95 (s, 4 F), –122.74 (s, 2 F), –126.15 (s, 2 F), –157.79 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{44}H_{26}BN_3O_3F_{17}$: 977.1827; found: 977.1830.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 380 (13), 466 (1), 496 nm (1.3).

Fluorescence (CH_2Cl_2, λ_{ex} = 380 nm): λ_{max} = 549 nm, Φ_F = 0.09.

β-Mono(tri/tetrafluorobenzo)-*meso*-triarylsubporphyrins; General Procedure

Subporphyrin **8b** (20 mg, 27.6 μmol) was dissolved in DMSO (8 mL) and heated to 100 °C, then $Na_2S_2O_4$ (0.27 mmol) and K_2CO_3 (0.27 mmol) were added; the resulting solution was stirred for 15–30 min under a N_2 atmosphere (monitored by TLC). The mixture was cooled to r.t., then it was diluted with CH_2Cl_2 (30 mL) and passed through a short column (silica gel). The filtrate was washed with H_2O (3 ×), dried (anhyd Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2–hexane–Et_2O, 1:15:1) to give the product.

Subporphyrin 12a

From subporphyrin **8b** (12 mg, 16.6 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:15:1), to give **12a** (9.5 mg, 85%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (br s, 2 H, β-H), 8.16 (d, *J* = 4.4 Hz, 2 H, β-H), 8.08 (d, *J* = 7.2 Hz, 2 H, *o*-H_{Ph}), 7.84 (t, *J* = 4.8 Hz, 2 H, *p*-H_{Ph}), 7.65–7.75 (m, 7 H, *m*,*p*-H_{Ph}), 7.52 (m, 2 H, *o*-H_{Ph}), 7.33 (m, 2 H, *o*-H_{Ph}), 7.19 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.89, 142.34, 138.56, 138.50, 137.54, 137.48, 137.28, 137.23, 136.44, 133.10, 133.01, 131.50, 128.80, 128.38, 128.29, 128.08, 127.29, 127.19, 123.96, 123.12, 122.92, 121.99, 119.30, 118.48, 105.12, 104.88, 104.61.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –104.54 (m, 1 F), –133.64 (dq, J_1 = 22.2 Hz, J_2 = 5.3 Hz, 1 F), –135.00 (m, 1 F), –156.88 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{37}H_{20}BN_3F_3$: 573.1733; found: 573.1731.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 378 (25), 464 (1.5), 488 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 378 nm): λ_{max} = 505, 534 nm, Φ_F = 0.09.

Subporphyrin 12b

From subporphyrin **8b** (12 mg, 16.6 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:15:1), to give **12b** (0.6 mg, <5%) as an orange solid.

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{37}H_{21}BN_3F_8$: 669.1732; found: 669.1741.

Subporphyrin 13a

From subporphyrin **9b** (16 mg, 17.2 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:20:1), to give **13a** (11 mg, 80%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (br s, 2 H, β-H), 8.20 (d, 2 H, β-H), 8.17 (m, 2 H, *o*-H_{Ph}), 8.02 (m, 4 H, *m*-H_{Ph}), 7.84 (m, 2 H, *m*-H_{Ph}), 7.79 (m, 2 H, *o*-H_{Ph}), 7.44 (m, 2 H, *o*-H_{Ph}), 7.26 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.92, 142.37, 141.05, 141.01, 140.82, 139.94, 138.86, 138.76, 133.49, 133.26, 131.89, 131.07, 130.95, 130.77, 130.63, 125.97, 125.94, 124.56, 124.52, 124.48, 123.40, 123.20, 122.69, 122.37, 118.18, 117.44, 105.91, 105.68, 105.40.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.34 (s, 6 F, CF_3), –62.48 (s, 3 F, CF_3), –104.00 (m, 1 F), –132.14 (m, 1 F), –134.54 (m, 1 F), –156.83 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{40}H_{17}BN_3F_{12}$: 777.1355; found: 777.1361.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 376 (11), 466 (1.2), 490 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 376 nm): λ_{max} = 511 nm, Φ_F = 0.09.

Subporphyrin 13b

From subporphyrin **9b** (16 mg, 17.2 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:20:1), to give **13b** (0.8 mg, <5%) as a yellow solid.

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{40}H_{18}BN_3F_{17}$: 873.1353; found: 873.1342

Subporphyrin 14

From subporphyrin **10a** (20 mg, 25.2 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:20:1), to give **14** (14.1 mg, 78%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.4 Hz, 1 H, β-H), 8.47 (s, 1 H, H_{Ph}), 8.35 (s, 1 H, H_{Ph}), 8.31 (d, *J* = 4.8 Hz, 1 H, β-H), 8.28 (d, *J* = 4.4 Hz, 1 H, β-H), 8.23 (d, *J* = 4.4 Hz, 1 H, β-H), 8.17 (d, *J* = 4.4 Hz, 1 H, β-H), 8.04 (m, 5 H, H_{Ph}), 7.76 (m, 4 H, H_{Ph}), 1.58 (s, 9 H, *t*-Bu), 1.54 (s, 9 H, *t*-Bu), 1.52 (s, 9 H, *t*-Bu).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.34, 151.12, 141.63, 140.79, 140.44, 139.87, 139.40, 138.52, 135.17, 133.90, 133.82, 132.77, 132.52, 129.72, 127.93, 125.90, 125.75, 123.28, 122.67, 122.26, 121.85, 120.27, 117.87, 111.59, 35.21, 34.83, 34.80, 31.48, 31.34.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –132.7 (d, *J* = 12 Hz, 1 F), –135.1 (d, *J* = 12 Hz, 1 F), –157.60 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{47}H_{43}BN_3F_2$: 697.3549; found: 697.3531.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 382 (10), 468 (1), 524 nm (1.5).

Fluorescence (CH_2Cl_2, λ_{ex} = 382 nm): λ_{max} = 549 nm, Φ_F = 0.07.

Subporphyrin 15a

From subporphyrin **11b** (18 mg, 21.8 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:5:1), to give **15a** (13 mg, 85%) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.4 Hz, 2 H, β-H), 8.15 (t, *J* = 4 Hz, 2 H), 8.01 (d, *J* = 8.4 Hz, 2 H, β-H), 7.83 (t, *J* = 4.4 Hz, 2 H), 7.26 (m, 4 H, *m*-H_{Ph}), 7.22 (d, *J* = 7.2 Hz, 2 H, *o*-H_{Ph}), 7.04 (d, *J* = 6 Hz, 2 H, *o*-H_{Ph}), 4.02 (s, 6 H, OMe), 4.00 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.11, 159.76, 142.77, 138.42, 134.09, 132.71, 132.46, 129.47, 128.78, 123.93, 123.04, 122.80, 121.92, 121.82, 118.59, 118.03, 114.47, 113.01, 112.64, 55.52, 55.43, 29.69.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –130.15 (d, *J* = 19.2 Hz, 2 F), –154.56 (d, *J* = 18.8 Hz, 2 F), –156.60 (m, 1 F, BF).

HRMS (MALDI TOF): *m*/*z* [M – F]$^+$ calcd for $C_{40}H_{25}BN_3O_3F_4$: 681.1956; 681.1947.

UV/Vis (CH_2Cl_2): λ (relative intensity) = 384 (14), 466 (1.7), 488 nm (1).

Fluorescence (CH_2Cl_2, λ_{ex} = 384 nm): λ_{max} = 537 nm, Φ_F = 0.08.

Subporphyrin 15b
From the subporphyrin **11b** (18 mg, 21.8 μmol), chromatography (CH_2Cl_2–PE–Et_2O, 1:5:1), to give **15b** (0.8 mg, <5%) as an orange solid.

HRMS (MALDI TOF): *m*/*z* $[M - F]^+$ calcd for $C_{40}H_{27}BN_3O_3F_8$: 759.2049; found: 759.2071.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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