

# A Review of the Synthetic Methods for Fluorinated Porphyrin Derivatives

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**ABSTRACT** : Synthetic methods for the fluorine-containing porphyrins at meso- or beta-positions are reviewed. Generally, the porphyrins with fluorine or fluorinated substituents at meso- or beta-positions could be prepared by the condensation of a proper fluorine substituted pyrroles with fluorinated aldehydes. Palladium mediated coupling of iodo or bromoporphyrins with the fluorinated-alkyl/aryl iodide resulted in fluorinated porphyrins. For the direct substitution of fluorine at meso-position, protioporphyrin was reacted with cesium fluoroxysulphate or N-fluoropyridinium triflate as electrophilic fluorine source.

**KEYWORDS** – Porphyrin, Fluorine, Metalloporphyrin

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## I. INTRODUCTION

Porphyrins (PP) are a group of macro-heterocyclic compounds, consisting of four pyrrole rings joined by four methinic carbons. A total of 26 conjugated  $\pi$ -electrons are delocalized on the planar macrocyclic ring thus cause to represent their aromaticity. They have absorption in long wavelength of light thereby representing characteristic colors. The name "porphyrin" derives from the Greek word porphyra, meaning purple [1]. Porphyrins easily converted to metalloporphyrins by complexing with metal ions, Mg, Fe, Zn, Ni etc. Porphyrin and its derivatives play multiple roles in nature, such as light absorption, oxygen carriage and energy transfer. These features enable their application in the field of optoelectronics, solar cells and photodynamic therapy (PDT) [2]. The structural modeling and synthesis of new porphyrins has been grown in order to modify electronic and biophysical properties of PP. It has been known that the addition of fluorinated substituents in the porphyrins could improve the electrical and magnetic properties, photostability and biophysical properties [3-5]. Fluorine is the most electronegative and the second smallest atom. This combination of small steric influence and an outsized electronic effect enable the modulation of their electronic properties of porphyrins avoiding significant structural deformations [5]. Among the most predictable changes in the properties of porphyrin derivatives by fluorination include (1) an increase in oxidative stability, and (2) a decrease in ring nitrogen basicity providing in more Lewis-acidic and electron-deficient condition, and (3) the alteration of their physicochemical properties [5,6]. The effect of fluorination upon porphyrin's chemical and physical properties depends strongly upon the position of the fluorine substituent and the type, number, and location of the remaining substituents. Various derivatives of PP with fluorine substitution at specified position are important in designing of PP aiming in specific applications. Thus, efficient synthetic methods for tailor-made fluorinated PP are demanded in electrochemical, photodynamic and pharmaceutical research field. Here, the synthetic techniques for preparation of fluorinated porphyrins are surveyed.

## II. SYNTHESIS OF FLUORINATED PORPHYRINS

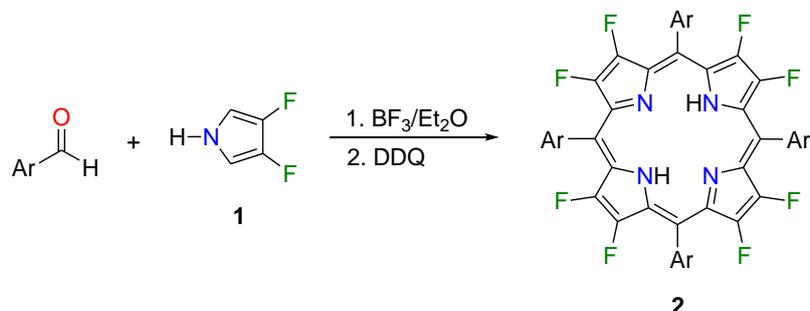
One of the most convenient methods for porphyrin synthesis is the acid catalyzed condensation of pyrrole with specific aldehyde, followed by oxidation of the porphyrinogen [7]. The relative simplicity of this method has driven to large scale preparation of tetraarylporphyrins. Lindsey [8] improved condensation-oxidation procedure available in higher yields, milder conditions relying Lewis acid (TFA or  $\text{BF}_3$ ) catalyst. Later, substituted asymmetrical porphyrins (A3B, A2B2, A2BC) were obtained via mixed aldehyde condensations as starting materials [9]. Many of synthetic approaches to the fluorinated porphyrins have been exponentially reported. Here, we review the fluorination of porphyrin derivatives in two categories: the first is the condensation of fluorinated pyrrole or fluorinated aldehyde, second one is the introduction of fluorine or fluorinated substituent into the preformed porphyrins at the meso- or beta-positions.

### 2.1 Fluorine Substitution at $\beta$ -Position

The fluorinated porphyrins at beta-position include  $\beta$ -fluoro-porphyrins and porphyrins containing fluoroaryl or fluoroalkyl substituents in the  $\beta$ -position.

### 2.1.1 Directly Connected $\beta$ -Fluoroporphyrins

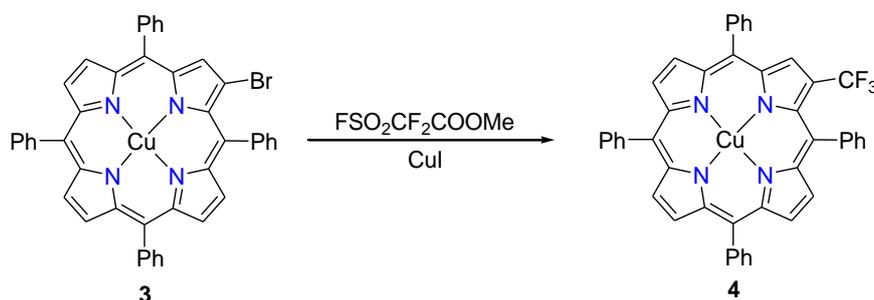
Synthetic methods of  $\beta$ -fluorinated porphyrins are well established. Ogoshi and Suzuki reported  $\beta$ -fluorinated porphyrins using the condensation of fluorine-substituted pyrrole or fluorinated dipyrrolylmethane with a proper aldehyde resulting in  $\beta$ -fluorinated porphyrin [10]. Later, Lindsey [11] established one-pot process features a Lewis acid-catalysed ( $\text{BF}_3$ ) condensation of aldehydes with pyrrole followed by oxidation. It turned out as the most common pathway for the synthesis of  $\beta$ -fluorinated porphyrins. For instance, beta-octafluoroporphyrin **2** was prepared from by the Lindsey's condensation of the corresponding aldehydes with 3,4-difluoropyrrole **1** as in scheme 1 [12,13].



**Scheme 1.** The condensation-oxidation method for  $\beta$ -octafluorotetraarylporphyrin

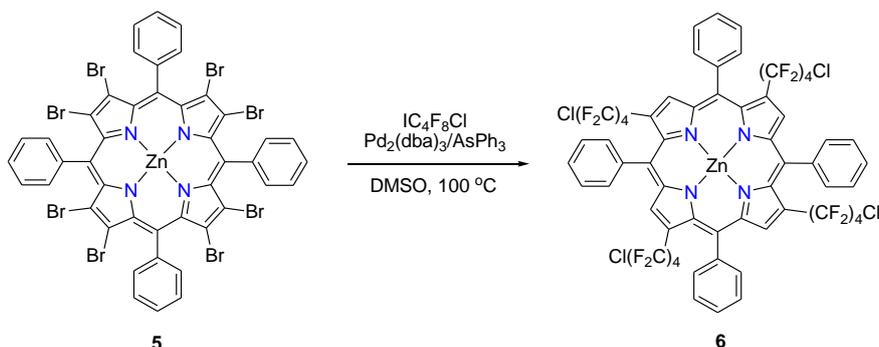
### 2.1.2 Fluoroalkyl at $\beta$ -Position

Trifluoromethyl group is a representative fluoroalkyl group showing the maximum electron withdrawing effect among one carbon. Thus, introduction of  $\text{CF}_3$  group had been attracted in medicinal and electronic material industry expecting a unique electrostatic effect [14]. Direct introduction of  $\text{CF}_3$  at beta-position was achieved by Chen using palladium catalyzed coupling of copper(II) incorporated beta-bromoporphyrin **3** with methyl difluoro(fluorosulfonyl)acetate ( $\text{FSO}_2\text{CF}_2\text{COOMe}$ ) in the presence of  $\text{CuI}$  [15].



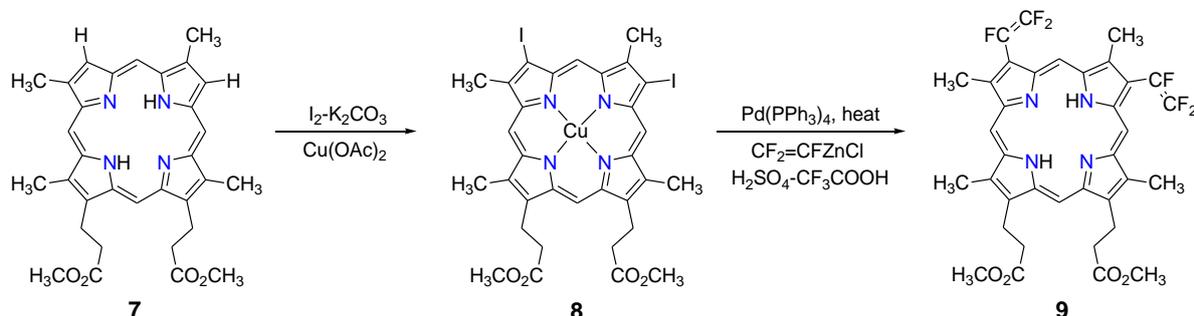
**Scheme 2.** Pd-catalyzed  $\text{CF}_3$  coupling of  $\beta$ -bromoporphyrin

Unfortunately, Lindsey's method for the synthesis of  $\beta$ - $\text{CF}_3$ -PP from 3,4-ditrifluoromethylpyrrole was unsuccessful. The electrophilic aromatic substitution of 3,4-ditrifluoromethylpyrrole was retarded due to the extremely electron-withdrawing effect of  $\text{CF}_3$  groups in pyrrole [3]. Several reports of perfluoroalkylation of porphyrin by halogen substitution have appeared [16]. Perfluoroalkylation from  $\beta$ -octabromoporphyrins **5** by Pd-catalyzed cross-coupling is reported to be efficient and easy to isolation of sterically hindered perfluoroalkylated porphyrin derivatives **6a** in Scheme 3, [17].



**Scheme 3.** Pd-catalyzed perfluoroalkylation of  $\beta$ -bromoporphyrin

Kumadaki and coworkers[18] also reported the introduction of perfluorovinyl group at beta-position using palladium catalyzed coupling of iodoporphyrin **8** with trifluorovinylzinc chloride. To the copper complex of 3,8-diiododeuteroporphyrin dimethyl ester **8**, which is obtained from deuteroporphyrin dimethyl ester **7**, was added fluorovinylzinc chloride added in acidic media, and then reflux yielded 3,8-bis(trifluorovinyl)porphyrin (**9**).



Scheme 4. Pd-catalyzed perfluorovinylation of  $\alpha$ -iodoporphyrins

## 2.2 Meso-Fluorinated Porphyrin

In traditional acid-catalyzed macrocycle syntheses, the variation of substituents at the porphyrin meso-position is limited largely by the lack of appropriate starting aldehyde. For instance, fluoro-PP at meso position could not be prepared because it is extremely difficult to obtain formyl fluoride. Thus, direct fluorination of PP at meso-position was tremendously studied focused on the relevant fluorine source. Meanwhile, the introduction of fluoroalkyl or fluoroaryl group at meso-position have been proceeded via several methods.

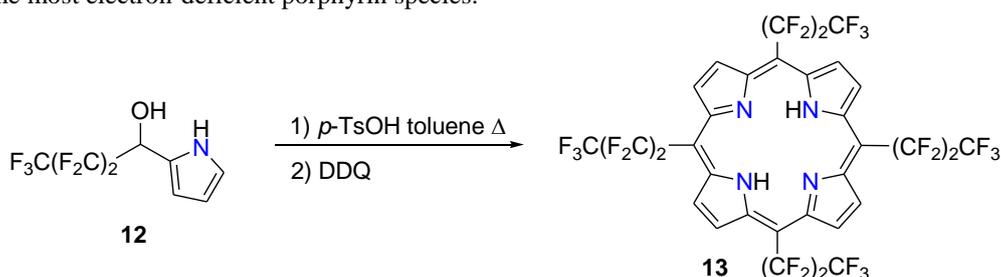
### 2.2.1 Directly Connected Meso-Fluorine

Directly fluorine connected porphyrin at meso-position was successfully synthesized via electrophilic fluorination using electrophilic fluorination agents such as cesium fluoroxysulphate ( $\text{CsSO}_4\text{F}$ ) [19] and N-fluoropyridinium triflate (Scheme 5)[20]. It is notable that all the beta-position of PP should be blocked against electrophilic fluorine, otherwise beta-fluorination was inevitable. Several meso-fluoroporphyrin derivatives have also been prepared in this manner[21, 22].

Scheme 5. Direct fluorination of porphyrin at meso-position

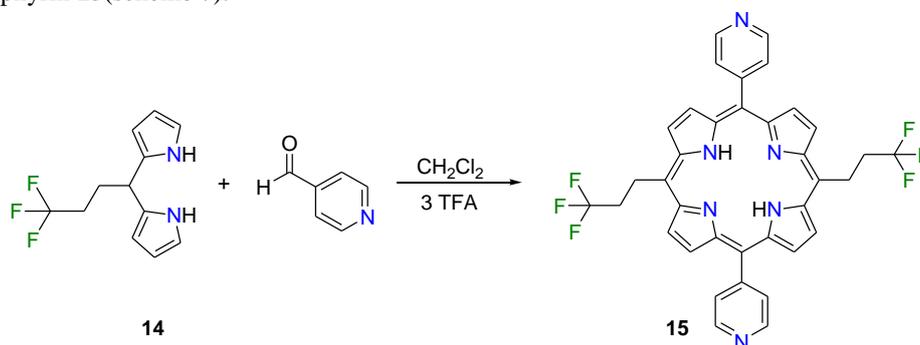
### 2.2.2 Meso-Fluoroalkyl Porphyrins

A pioneer in the area of porphyrin synthesis, DiMaggio developed a modified condensation methodology that enabled the facile, high yield synthesis of perfluoroalkyl connected porphyrin **13** at meso-positions (Scheme 6)[23]. It turned out that those meso-perfluoroalkylporphyrins represented themselves in a class of the most electron-deficient porphyrin species.



Scheme 6. Synthesis of fluoroalkylated porphyrin at meso-position

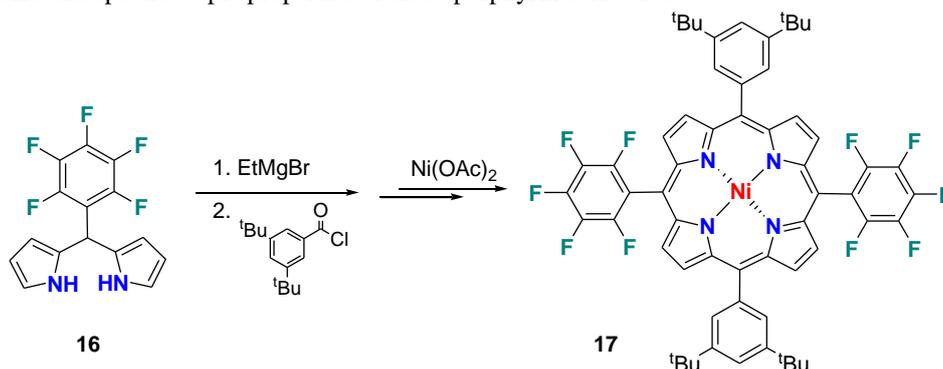
The condensation of fluorinated bispyrrole with the corresponding aldehyde resulted in the synthesis of meso-fluoroalkyl containing PPs. The bispyrrole **14**, derived from the condensation of butanal with excess pyrrole in the presence of and TFA, was reacted with pyridine carboxaldehyde in a stoichiometric amount to yield the porphyrin **15** (scheme 7).



Scheme 7. Synthesis of fluorinated porphyrin at meso-position

### 2.2.3 Meso-Fluoroaryl Porphyrins

Hwang and co-workers [24] prepared the perfluoroaryl substituted porphyrins at meso-position using a typical Lindsey method. The condensation of pentafluoroaryl bispyrrole **16** with alkyl-substituted benzaldehyde generated porphyrin, then subsequent treatment with Ni<sup>+2</sup> ion resulted A2B2-type metalloporphyrin **17** in 55% yield. They prepared various fluorinated A2B2 porphyrins from the fluoro-bispyrrole and characterized the photoelectronic and spectroscopic properties of those porphyrin derivatives.



Scheme 8. Synthesis of perfluoroaryl substituted porphyrin at meso-position

### 2.2.4 Fluoroalkoxy Porphyrins at Meso

The palladium mediated cross-coupling reported by Zhang could be used for fluoroaryloxy porphyrins [25]. By adapting of the palladium mediated cross-coupling, diverse fluoroalkoxy-substituted dipyrrolyl porphyrins were synthesized by Vulpe [26] as in scheme 9. Initially, 5,15-dipyrrolyl porphyrin was brominated with porphyrin NBS in chloroform to give bromo-PP **18** and then coupled with the corresponding fluoroalcohols under Pd<sub>2</sub>(dba)<sub>3</sub>-Cs<sub>2</sub>CO<sub>3</sub> to give alkoxy porphyrin **19**. Similarly, a series of fluorine rich porphyrins **C4F6-C10F18P** were prepared (Fig. 1).

Scheme 9. Palladium catalysed synthesis of fluoroalkoxy-5,15-dipyrrolyl porphyrin

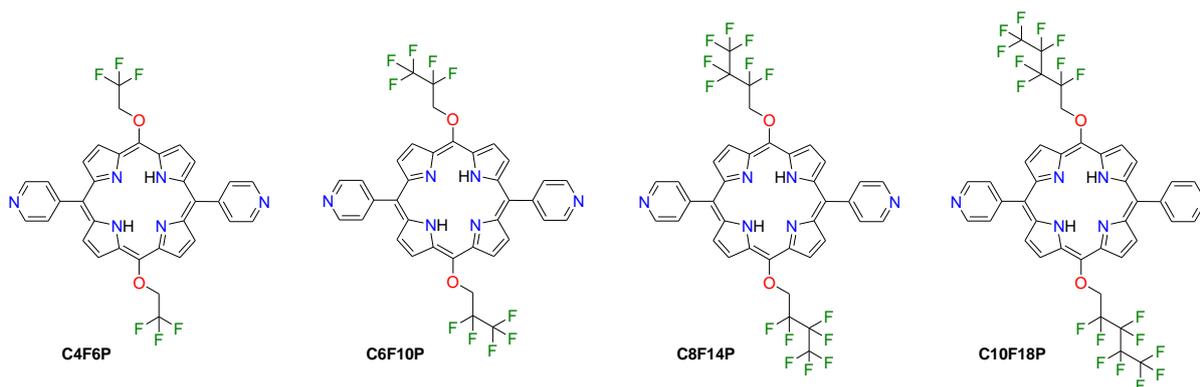
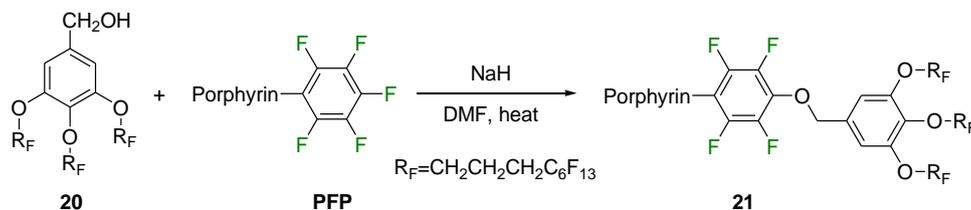


Figure 1: Fluoroalkoxy-substituted 5, 15-dipyridylporphyrins.

### 2.2.5 Meso-Alkoxyfluoroaryl Substituted Porphyrins

Fluorinated aryl substituents could be used to synthesize dendritic porphyrin assemblies [27]. Nucleophilic aromatic substitution at the para-position of tetrakis(pentafluorophenyl)porphyrin (**PFP**) has been used as a general method for preparing porphyrin containing dendrimers. Briza and coworkers utilized connection of pre-formed 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin **PFP** with fluorinated phenoxy group **20** (Scheme 10) to afford dendrimer (**21**).



Scheme 10. Porphyrin connected dendrimer

## III. APPLICATIONS AND PROPERTIES OF FLUORINATED PORPHYRINS

### 3.1 Photochemical Properties

Addition of fluorine or fluorinated substituent into porphyrins endow them many of different properties that could not be observed in non-fluoroporphyrins because of the variation of electron density. For instance, the UV absorption and emission of **FPP** [tetrakis(pentafluorophenyl)porphyrin] are different to those of non-fluoroporphyrin **TPP** (tetrakisphenylporphyrin). The band gap values of those derivatives are altered from 1.85 to 2.06 eV [24]. Those changes attribute to the fluorine-induced alteration of molecular orbital energy.

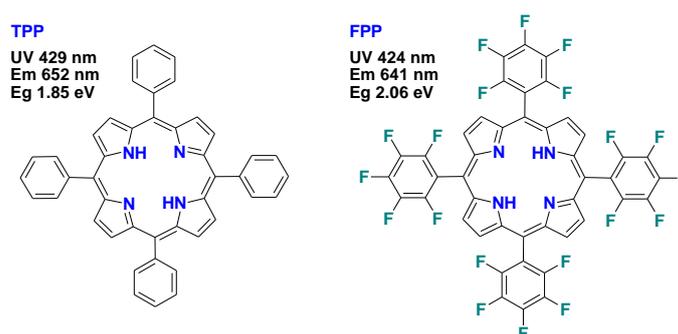


Figure 2: Spectroscopic properties of TPP and FPP.

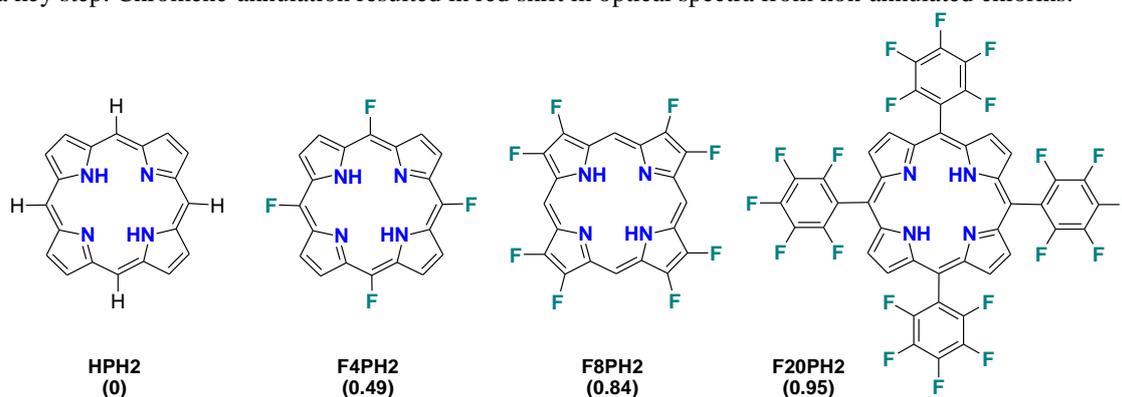
### 3.2 Ionization Potential

Fluorination of a molecule directly affects its electronic stability. Cationic species are destabilized by electron withdrawing and stabilized by electron donation. Fluorine substituents on the porphyrin ring shift ring redox potentials to the positive. Because the ionization is retarded by fluorine addition, the ionization potential (IP) of porphyrin increases upon fluorination. More systematic studies have been performed to obtain the relationship between fluorination and porphyrin's electronic properties [28]. The calculation and experimental data showed that meso-substitution has a greater effect on the porphyrin ring than the  $\beta$ -substitution. The IP value of 5,10,15,20-tetrafluoroporphyrin (**F4PH2**) is about 0.49 eV higher than that of **HPH2**, and  $\beta$ -

octafluoroporphyrin (F8PH2) shows 0.84 eV higher IP value than that of HPH2 (Fig. 3). In overall, the effect appeared in  $\beta$ -perfluorination is roughly comparable to the effect of perfluorination in tetraphenylporphyrin, shifted to positively 0.95 eV in F20TPPH2[4]. It is considered that the fluorine mediated inductive effect is dependent with the distance between fluorine and effecting target atoms.

### 3.3 Physiochemical Properties

Introduction of fluorine or fluorinated functional group into porphyrins result in interesting properties that are adequate for optical sensor, solar cell applications. For instance, fluorinated Pt(II) porphyrins show improved hydrophobicity and enhanced oxidative stability, thereby they are utilized as luminescent dyes in the field[29]. In addition, the use of pentafluorophenyl groups on the porphyrin meso-position has permitted the direct functionalization of the porphyrin through  $S_NAr$  reactions. This synthetic method provided a route to diverse porphyrin derivatives possessing different physiochemical properties from the origin. For instance, Bruckner [30] reported the synthesis of chromene-annulated (pentafluorophenyl)chlorins from tetrakis(pentafluorophenyl)-porphyrins F20PH2 by an intramolecular nucleophilic aromatic substitution reaction as a key step. Chromene-annulation resulted in red shift in optical spectra from non-annulated chlorins.



**Figure 3:** Ionization potential and abbreviations of fluorinated porphyrins with (IP value).

## IV. CONCLUSION

Fluorinated porphyrins have diverse properties different from those of origin porphyrins such as photochemistry, oxidation-reduction potential and physiochemical stability. Introduction of fluorine or fluorinated functional groups into porphyrin could be processed via case-fit methods. Directly fluorinated or fluoroalkylated porphyrins at beta-position are able to be synthesized by the condensation of 3,4-difluoropyrroles with the corresponding aldehydes. In similar to beta-substitution, condensations of the aldehyde containing fluorinated group with the pyrrole give meso-fluorinated porphyrins. For the direct substitution of fluorine at meso-position from the meso-protoporphyrin, cesium fluoroxy sulphate or N-fluoropyridinium triflate were applied.

## V. ACKNOWLEDGEMENTS

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