Introduction of Carboxylic Ester and Acid Functionalities to *meso*-Tetrakis(pentafluorophenyl)porphyrin and their Limited Electronic Effects on the Chromophore

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Abstract

Alkyl- or aryl-carboxylic acid-functionalized porphyrinic dyes are sought after because of their propensity to adhere strongly to many metal oxide surfaces as required for their application as, for instance, sensitizers in dye-sensitized solar cells (DSSCs), in air purification, or chemosensing systems. The S_NAr reaction of the pentafluorophenyl group is a versatile method to introduce functionality into *meso*-pentafluorophenyl-substituted porphyrins. The conditions to introduce one through four alkyl- or aryl-carboxyl functionalities using mercaptopropionate or 3,4-dihydroxybenzoate esters, respectively, are explored, and the regioisomeric products are spectroscopically characterized. Their saponification to the corresponding carboxylic acids was studied. By experimental determination of their optical properties (absorption and emission spectroscopy) and their frontier orbital positions by cyclic voltammetry, we demonstrate the minimal electronic influence this derivatization method has on the chromophore.

1. Introduction[‡]

Solid phase-bound porphyrins may find use in in dye-sensitized solar cells (DSSCs)[1-3], other hybrid electronics,[4] air purification applications,[5] the generation of antimicrobial surfaces,[6] in catalysis,[7] and sensing systems.[8] All these applications will benefit from versatile strategies to establish carboxyl groups that have the ability to anchor the chromophore well to a wide range of solid oxide surfaces,[4] perhaps even in defined orientations.[9]

[‡] Abbreviations: DSSC: dye-sensitized solar cell; T^FPP: *meso*-tetrakis(penta-fluorophenyl)porphyrin;

Porphyrin derivatives have emerged as the highest-efficiency dyes in DSSCs.[10-13] Key to the increase of efficiency in porphyrin-based DSSCs was the development of non-aggregating porphyrins with high extinction coefficient absorption spectra reaching into the NIR, such as push-pull architecture porphyrin **1** or π -extended porphyrin **2**. [10, 14, 15] However, the syntheses of these and related systems is complex and inefficient, inhibiting the progress in the understanding of the correlation of molecular design and photovoltaic performance by testing a wider range of derivatives that might include a range of commercially viable porphyrinoid dyes,[16] or hydroporphyrins, nature's light harvesters.[17] Recently tested hydroporphyrins were promising but they were also prepared by multi-step, non-trivial total syntheses.[18]

(Structures **1** and **2**)

Irrespective of the type of dye, carboxylic acid groups are by far the most common anchoring group for dye attachment to TiO₂ or other metal oxide surfaces.[1, 4, 9, 19] However, from a practical point of view, the synthesis of porphyrinoid dyes with a single or multiple carboxylic acid groups is associated with practical difficulties since conventional bulk silica gel column chromatography techniques are difficult to apply to (poly)carboxylates. This suggests the unveiling of the carboxyl functionality at a very late stage of the dye synthesis, such as by synthesis of protected carboxyl derivatives that are deprotected directly prior to attachment to the semiconductor.[20] Alternatively, the carboxyl group is introduced to the dye at a late – ideally final – synthetic stage.

Dyes containing pentafluorophenyl (C₆F₅) groups are particularly appealing in this context.[21] Many *meso*-(C₆F₅)-substituted porphyrinoids are literature-known,[21-24] including

N-fused and confused porphyrin **3** and the porpholactone-based halochromic sensor for high pH values **4**,[17] other chemosensors and chemophototherapeutics,[25-31] and detailed studies of their electron injection dynamics into semiconductor surfaces have become known.[32] The (C₆F₅)-groups impart excellent solubility to the porphyrinoids and are believed to also protect the chromophores from oxidative degradation.[33] The parent porphyrins, *meso*-tetrakis(pentafluorophenyl)porphyrin (T^FPP, **5**) is well known and commercially available.[13]

(Structures **3** and **4**)

Crucially, the (C₆F₅)-group on porphyrin **5** and related porphyrins is susceptible to a highly selective and mild reaction, a S_NAr reaction of the *para*-F group with a soft nucleophile, such as a thiol, amine, alcohol, azide, or catechol.[27, 28, 30, 31, 34-43] Using carboxylic acid-appended soft nucleophiles, one can conceivably prepare carboxylic acid-bearing derivatives, thus enabling the attachment of the dye to the metal oxide surface (Scheme 1). We also note that, in principle, the optimization of the reaction conditions of this (C₆F₅)-modification approach may allow it to be inverted, i.e., a semiconductor surface modified with a suitable nucleophile might allow the attachment of a *meso*-(C₆F₅)-substituted dye. Either of these two post-chromophore synthesis modification strategies will allow the testing of a larger number of (C₆F₅)-substituted porphyrinoid dyes as sensitizers in DSSCs or other applications than would be possible relying on *de novo* syntheses of carboxyl-substituted dyes. Also, the field of the organization of porphyrins at solid interphases may benefit from the ability to introduce carboxylate functionalities to the porphyrins in a final post-chromophore modification step.[44]

(Scheme 1)

From literature precedents,[43] we identified the reagents mercaptopropionate and 3,4-dihydroxybenzoate as readily available and promising nucleophiles to introduce alkyl- or aryl-carboxyl functionalities, respectively. Which reagent is the most practical for the introduction of carboxyl groups? Is it possible to introduce one to four carboxylates? Can the esters be purified and the corresponding carboxylic acid be prepared by deprotection (saponification)? And importantly, will the introduction of one to four thiols or catechols to the (C₆F₅)-groups affect the electronic structure of the chromophore? We will report here the results of a study aimed at providing answers to these questions.

In short, one to four carboxylates can indeed be introduced into a (C₆F₅)-substituted porphyrin and the products were spectroscopically characterized, whereby the combination of ¹H and ¹⁹F NMR spectroscopy proved particularly useful for the identification of the products. The effects on the electronic structure of the chromophores were probed using UV-vis and fluorescence spectroscopy and cyclic voltammetry, and found to be small. The binding of the deprotected carboxylic acids to TiO₂ and SnO₂ nanoparticles was demonstrated, generally highlighting the utility of the method toward the synthesis of porphyrinic chromophores designed to adhere to solid oxide surfaces.

2. Results and Discussion

2.1 The Synthesis of T^FPP Modified with Carboxylic Acids and Esters

Reaction of T^FPP (**5**) with ~6 equiv ethyl mercaptopropionate (**11**) under conditions described for other S_NAr reactions using thiols (DMF, Et₂NH, ambient temperature) formed within 0.5 h a number of products of higher polarity than the starting material (Scheme 2).[38-40] Flash

column chromatography allowed the separation of four fractions, one of which could be further separated into two using preparative plate chromatography. Their HR-MS (ESI+) spectra confirmed their compositions corresponding to the products **6a** through **6d**, carrying one to four ethyl mercaptopropionate functionalities. Two fractions indicated that two F-to-thiol substitutions had taken place, as expected for the formation of a *cis*- and *trans*-isomer of **6b**. The use of only 1 equiv or stoichiometric excess of methyl propionate increased the fraction of the mono- and tetra-substituted derivatives **6a** and **6d**, respectively.

(Scheme 2)

The combination of ^1H and ^{19}F NMR spectra of all products allowed their unambiguous characterization (Figures 1 and 2). The ability to record well-resolved ^{19}F NMR spectra of the (C_6F_5)-derived porphyrins are an added benefit of perfluorophenyl-substituted porphyrinoids, though the ability to record ^{13}C NMR spectra is somewhat compromised due to the couplings with the fluorine atoms.[21]

The ^1H NMR spectra of **6a** through **6b** show the presence of the ethyl mercaptopropionate groups and the relative integrations of the β -hydrogens and those of the ethyl mercaptopropionate allow a clear determination of the number of substitutions that have taken place. The distinction of the bis-substituted isomers of **6b** is based on the coupling pattern observed in the β -region of the ^1H NMR spectrum: two d for the (idealized) $\text{C}_{2\text{h}}$ -symmetric **6b^{trans}**; two d and two (overlapping) s for the (idealized) $\text{C}_{2\text{v}}$ -symmetric isomer **6b^{cis}**.

(Figure 1)

The coupling patterns observed in the ^{19}F NMR spectrum of **6a** through **6b** show clearly that selectively only the *p*-F was substituted, as expected. The relative integrations of the F-signals corresponding to intact C_6F_5 -groups and substituted $\text{C}_6\text{F}_4\text{SR}$ -groups also show the degree of substitution, but the ^{19}F NMR spectrum could not distinguish between the *cis* and *trans*-isomers of disubstituted derivative **6b**.

(Figure 2)

Much to our disappointment, the saponification of the ethyl ester to generate the carboxylic acid under a number of reaction conditions (KOH or LiOH, different solvents and temperatures) failed in our hands. Instead, it lead to a breakage of the $\text{S-C}_{\text{alkyl}}$ bond and the generation of (C_6F_4 -*p*-SH)-derivatives. Thus, while the method to derivatize T^{F} PP **5** with ester functionalities was successful, and the esters may find some use, they were of no use for the preparation of the deprotected carboxylic acids. On the other hand, the use of 1.0 equiv of mercaptopropionic acid resulted in the formation of the mono-carboxylated product **7a** in good yield (60%), whereas, the reaction of **5** with an excess of mercaptopropionic acid resulted in the formation of tetra-substituted product **7d** in acceptable yield (40% yield), with the remainder being mostly bis- and tris-substituted products.

The reaction of a catechol derivative with T^{F} PP **5** leading to a substitution of two fluorine atoms on the (C_6F_5)-groups was described previously.[43] We applied this reaction to ethyl 3,4-dihydroxybenzoate **10**. Indeed, reaction of T^{F} PP **5** with ~6 equiv of **10** in the polar green solvent *N*-methylpyrrolidine (NMP) in the presence of an inorganic base (K_2CO_3) at 100°C over the course of ~2h resulted in the formation of four products **8a** through **8d**, containing one through

four catechol ester moieties (as per ESI+ MS) (Scheme 2). Presumably, the *cis*- and *trans*-isomers of **8b** are also formed but we could not separate them or even unambiguously detect their presence.

In general, β -proton signal in the ^1H NMR spectrum shows the change of the symmetry of the molecule, and the relative integration ratio of this signal to that of the catechol protons (at 7.0-8.0 ppm) indicates the number of catechols present (Figure 3). However, the signal splitting patterns are more complex than expected, often resulting in a split of the signal into a set in a 1:2 ratio, suggesting the presence of two isomers.

(Figure 3)

The regioisomers arise from the lack of complete regioselectivity of the reaction of the mono-substituted catechol with the C_6F_5 -group (Scheme 3). The *p*-F atom is the most activated toward the $\text{S}_{\text{N}}\text{Ar}$ reaction and will be substituted first, followed by one of the two equivalent *m*-F atoms. However, the nucleophilicity of the two non-equivalent catechol oxygens may not be sufficiently differentiated by the electronic influences of the catechol substituents, such as the carboxylic acid ester group present here. Thus, the first $\text{S}_{\text{N}}\text{Ar}$ displacement reaction may be caused by the 3-OH group, while in another case the 4-OH group may begin the reaction sequence, leading to the formation of regioisomeric products. We deduce from the Hammett ρ -factors for the OH group that the *p*-OH (4-OH) group is slightly more acidic (and therefore likely also a better nucleophile) than the *m*-OH (3-OH) group.

(Scheme 3)

The ^{19}F NMR spectra of the catechol-substituted compounds **8a** through **8d** also show the presence of isomers, particularly clearly shown in the split of the signal for the *o*-F closest to the catechol (Figure 4). All other signals simply exhibit much more complex coupling patterns as expected. Again, the ^{19}F NMR spectra are most diagnostic for the determination of the regioselective substitution of one *p*- and adjacent *m*-F atom in the C_6F_5 -group.

(Figure 4)

The LiOH-mediated saponification of the ester functionality of monoester **8a** in wet THF at elevated temperatures went smoothly and in essentially quantitative yields, generating acid **9a** that possessed all expected spectroscopic properties. This monoacid proved amenable to normal phase chromatographic purification. Likewise tetraester **8d** can be cleanly and in high yields saponified, providing tetraacid **9d** that can be purified by brief silica gel chromatography whereupon it proved to be pure by ^1H and ^{19}F NMR spectroscopy.

2.2 The Electronic Structure of the T^{F} PP Derivatives Modified with Carboxylic Acids and Esters

To assess the electronic influence of the varying degrees of thiol- and catechol-substitutions on the porphyrin chromophore, we determined their UV-vis and fluorescence emission spectra and their reduction potentials by cyclic voltammetry (CV), and compared the data to literature-known data of the parent porphyrin **5**.^[21, 45] The comparison of representative spectra are shown in Figure 5 and all results are tabulated in Table 1. The optical spectra of the derivatives are, with only minor deviations, essentially identical to those of the parent unsubstituted T^{F} PP **5**, independently of whether the ester or the acid was considered. All the redox potentials are,

within the margin of error, also essentially identical (Figure 6). Thus, we can conclude that the substitution of the (C₆F₅)-groups did not shift the HOMO–LUMO gap or the absolute frontier orbital positions.

(Figure 5)

Table 1.

Com-Pound	Absorption/nm (log ϵ /M ⁻¹ cm ⁻¹)	Fluorescence Emission/nm (rel, I)	Reduction Potentials/V		
			$E_{red1}^{1/2}$	$E_{red2}^{1/2}$	ΔE
5	411 (5.64), 506 (4.41), 582 (3.78)	642, 707 (1:2)	-1.292	-1.753	0.46
6a	412 (5.82), 507 (4.53), 584 (3.69)	641, 706 (1:2)	-1.324	-1.740	0.42
6b^{trans}	413 (5.52), 507 (4.08), 585 (3.70)	642, 706 (1:2)	-1.324	-1.794	0.47
6b^{cis}	415 (5.88), 508 (4.59), 582 (3.84)	643, 706 (1:2)	-1.318	-1.734	0.42
6c	414 (5.69), 507 (4.34), 584 (3.30)	643, 707 (1:2)	-1.307	-1.728	0.42
6d	415 (5.87), 508 (4.59), 583 (3.84)	645, 707 (1:2)	-1.315	-1.727	0.41
7a	412 (5.29), 506 (4.15), 583 (3.65)	642, 707 (1:2)	-1.289	-1.703	0.41
8a	415 (5.37), 505 (4.25), 585 (3.81)	641, 708 (1:2)	-1.712	-1.761	0.42
8b	415 (5.10), 510 (3.91), 585 (3.45)	643, 707 (1:2)	-1.688	-1.758	0.42
8c	415 (5.49), 510 (4.40), 585 (3.92)	643, 707(1:2)	-1.712	-1.777	0.42
8d	415 (5.31), 510 (4.13), 585 (3.63)	644, 707 (1:2)	-1.769	-1.809	0.43
9a	413 (5.10), 506 (3.95), 583 (3.48)	641, 707 (1:2)	-1.313	-1.703	0.43

(Figure 6)

2.3 The Binding of the Acid Derivatives to Semiconductor Surfaces

Dissolving the alkyl and aryl monoacids **7a** and **9a**, respectively, in EtOH/CH₂Cl₂ (final porphyrin concentration ~1 mM) and immersing an FTO-modified glass slide covered with a thin layer of TiO₂ or SnO₂ nanoparticles for 24 h at ambient temperature—standard conditions in the assembly of DSSCs—allows the porphyrin acids to adhere to the metal oxide surfaces, as immediately indicated by the dark brown colors of the metal oxide layers. Moreover, the UV-vis spectra of the solid samples prepared in dilute solutions indicate that the color arises from the porphyrins (Figure 7).

(Figure 7)

3. Conclusions

In conclusion, the introduction of one to four ester functionalities to (C₆F₅)-derived porphyrin **5** using ethyl mercaptopropionate (**11**) or ethyl 3,4-dihydroxybenzoate (**10**) is facile under mild reaction conditions. All possible products ranging from the mono- to the tetra-substituted derivatives can be formed, isolated, and unambiguously spectroscopically characterized, wherein ¹⁹F NMR is a very helpful tool. The right reaction conditions can be tuned such that the mono- or the tetra-substituted products can be formed as the major products. The saponification of the ethyl mercaptopropionate derivatives failed to produce the corresponding acids, but the mono- and tetraacid was prepared by reaction of T^FPP **5** with mercaptopropionic acid (**12**). The saponification of the 3,4-dihydroxybenzoate derivatives is, however, successful and prepares the

corresponding acids in excellent yields.

This methodology thus allows the study of the influence of the type, number, and position of carboxylic acid groups on the photovoltaic performance of a given (C₆F₅)-derived porphyrin or, likely, also other porphyrinoids, whereby it is important to point out that the functionality to link the dye to a surface was introduced post-macrocycle synthesis. The porphyrins prepared here served as model compounds to optimize the synthetic strategies presented. We fully recognize that these porphyrins are likely ill suited as efficient dyes in DSSCs. For example, they do not adhere to the donor-porphyrin-acceptor architectures recognized to be beneficial for light-harvesting porphyrins.[1-3, 11]

Neither of the substitutions had an effect on the electronic properties of the porphyrin, as assessed by a comparison of their optical spectra and electrochemical reduction properties. Provided that the (C₆F₅)-groups have a significant electronic effect on the porphyrin chromophore,[21] this result when replacing up to 8 of the 20 fluorines is not self-evident. Alas, we would caution against translating this result to porphyrinoid pigments for which a large coplanarity of the *meso*-aryl substituents is known to take place, and for which a larger electronic influence of the aryl groups has to be assumed.[46, 47]

4. Experimental

4.1. General

All solvents and reagents used were reagent grade or better and were used as received. The analytical TLC plates used were Silicycle ultra pure silica gel 60 (aluminum backed, 250 μm)

and the preparative chromatography plates (1.0 mm silica gel on glass) used, both provided by Scientific Adsorbents Inc., Atlanta, GA. *meso*-Tetrakis(pentafluorophenyl)porphyrin (**5**) was obtained from Huhu Technology, Inc., San Diego, CA.

^1H , ^{19}F , and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 MHz instrument in the solvents indicated, and were referenced to residual solvent peaks. UV/Vis spectra were recorded on a Cary 50 spectrophotometer and fluorescence emission spectra on a Cary Eclipse fluorimeter. High and low resolution mass spectra were provided by the Mass Spectrometry Facility, Department of Chemistry, University of Connecticut.

Cyclic Voltammetry experiments were recorded on a CHI600D electrochemistry system with a standard three-electrode cell assembly. The supporting electrolyte was 0.1 M TBAPF₆ dissolved in dry CH₂Cl₂. Pt wires were employed as both working and counter electrodes; an Ag/Ag⁺ couple was used as the reference electrode. All concentrations of dye solutions were maintained at 1 mM, and scanned at a scan rate of 200 mV/s. Prior to scanning, the solutions were sparged 5~10 min with a stream of purified N₂.

Transparent TiO₂ thin films were fabricated on microscope slides by spin coating 100 μL of TiO₂ paste (DSL 90-T, diluted 1:1 with terpineol) with a rotation speed of 1000 rpm for 30 s, followed by sintering at 500 °C for 30 min. The TiO₂ films were then dipped into 0.3 mM dye solutions in EtOH for 24 h. The films were then rinsed with EtOH twice to remove physisorbed dyes, and dried with a flow of N₂ at ambient T.

4.2. Reaction of 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (5**) with Ethyl**

3-Mercaptopropionate (**11**).

Reaction conditions adapted from the literature.[38-40] In a 50 mL round-bottom flask equipped with nitrogen line and a stir bar, T^FPP **5** (200 mg, 0.205 mmol) was dissolved in DMF (4 mL), diethylamine (Et₂NH, 100 μ l), and ethyl acetate (8 ml). To this was added ethyl 3-mercaptopropionate (**11**) (170 mg, ~6 equiv). Under N₂ and shielded from light with aluminum foil, the reaction mixture was stirred at ambient temperature. The disappearance of the starting material/appearance of the products was monitored by TLC. Once no further progress of the reaction was detectable (after ~1/2 h), the reaction mixture was reduced to dryness by rotary evaporation. The residue was taken up in CH₂Cl₂ (25 mL) and the organic phase was washed with distilled water (at least 3 $\times$ 100 mL). The organic layer was isolated, dried over Na₂SO₄, and reduced to dryness by rotary evaporation. A gentle stream of N₂ was passed over the residue for several h to ensure that it was thoroughly dried before it was purified by flash chromatography (silica gel–50%CH₂Cl₂/hexanes). Following the low polarity starting material **5** (~6.0 mg, ~3% recovery), four major fractions were isolated. The second fraction of **6b^{trans}** and **6b^{cis}** were isolated together (and subsequently separated using preparative plate chromatography using silica-25% hexanes/CH₂Cl₂).. Thus, the five major products **6a** (5%) **6b^{trans}** (30%), **6b^{cis}** (12%), **6c** (37%), and **6d** (13%) were isolated as dark purple solids. **6a**: R_f (silica-CH₂Cl₂/25% hexanes) = 0.85; ¹H NMR (400 MHz; CDCl₃): δ 8.97 (s, 6H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.56 (t, *J* = 7.0 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), -2.84 (s, 2H) ppm; ¹⁹F NMR (376 MHz; CDCl₃): δ -133.5 (dd, *J* = 25.2, 12.4 Hz, 2F), -136.5 (dd, *J* = 23.8, 8.1 Hz, 6F), -136.8 (dd, *J* = 25.2, 12.1 Hz, 2F), -151.3 (t, *J* = 20.8 Hz, 3F), -161.4 (td, *J* = 22.0, 6.9 Hz, 6F) ppm; ¹³C NMR (100 MHz; CDCl₃): δ 171.2, 104.7,

103.6, 61.2, 35.4, 29.9, 14.3 ppm; UV-vis (CH_2Cl_2) λ_{max} (log ϵ): 412 (5.82), 507 (4.53), 584 (3.69) nm; fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max} (rel. I) 641, 706 nm (1:2); HR-MS (ESI+, 1% $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$): calculated for $\text{C}_{49}\text{H}_{19}\text{F}_{19}\text{N}_4\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$, 1089.0900, found 1089.1000. **6b^{trans}**: R_f (silica- $\text{CH}_2\text{Cl}_2/25\%$ hexanes) = 0.48; ^1H NMR (400 MHz; CDCl_3): δ 9.00 (d, J = 4.6 Hz, 2H), 8.93 (d, J = 4.6 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.55 (t, J = 7.0 Hz, 2H), 2.94 (t, J = 7.0 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H), -2.86 (s, 1H) ppm; ^{19}F NMR (376 MHz; CDCl_3): δ -133.6 (dd, J = 25.1, 12.4 Hz, 2F), -136.5 (dd, J = 23.5, 8.0 Hz, 2F), -136.9 (dd, J = 25.3, 12.3 Hz, 2F), -151.4 (t, J = 20.9 Hz, 1F), -161.4 (td, J = 22.0, 6.8 Hz, 2F) ppm; ^{13}C NMR (100 MHz; CDCl_3): δ 171.2, 104.6, 103.5, 61.2, 35.4, 29.9, 14.3 ppm; UV-vis (CH_2Cl_2) λ_{max} (log ϵ): 413 (5.52), 507 (4.08), 585 (3.70), 595 (3.30) nm; fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max} (rel. I): 642, 706 nm (1:2); HR-MS (ESI+, 1% $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$): calculated for $\text{C}_{54}\text{H}_{28}\text{F}_{18}\text{N}_4\text{O}_4\text{S}_2$ $[\text{M}+\text{H}]^+$, 1203.1334, found 1203.1394. **6b^{cis}**: R_f (silica- $\text{CH}_2\text{Cl}_2/25\%$ hexanes) = 0.42; ^1H NMR (400 MHz; CDCl_3): δ 9.01 (s, 2H), 8.95 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.55 (t, J = 7.0 Hz, 2H), 2.94 (t, J = 7.0 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H), -2.84 (s, 1H) ppm; ^{19}F NMR (376 MHz; CDCl_3): δ -133.6 (dd, J = 25.4, 12.2 Hz, 2F), -136.5 (d, J = 15.6 Hz, 2H), -136.8 (dd, J = 25.4, 12.2 Hz, 2H), -151.4 (t, J = 20.8 Hz, 1H), -161.4 (t, J = 18.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz; CDCl_3): δ 171.2, 104.6, 103.5, 61.2, 35.4, 29.9, 14.2 ppm; UV-vis (CH_2Cl_2) λ_{max} , nm (log ϵ): 415 (5.88), 508 (4.59), 582 (3.84) nm; fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max} (rel. I): 643, 706 nm (1:2); HR-MS (ESI+, 1% $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$): calculated for $\text{C}_{54}\text{H}_{28}\text{F}_{18}\text{N}_4\text{O}_4\text{S}_2$ $[\text{M}+\text{H}]^+$, 1203.1334, found 1203.1297. **6c**: R_f (silica- $\text{CH}_2\text{Cl}_2/25\%$ hexanes) = 0.4; ^1H NMR (400 MHz; CDCl_3): δ 9.05 (s, 6H), 8.98 (d, J = 4.7 Hz, 2H), 4.33 (q, J = 7.1 Hz, 6H), 3.57 (t, J = 7.0 Hz, 6H), 2.96 (t,

$J = 7.0$ Hz, 6H), 1.40 (t, $J = 7.1$ Hz, 9H), -2.79 (s, 2H) ppm; ^{19}F NMR (376 MHz; CDCl_3): δ -133.6 (dd, $J = 25.0, 12.2$ Hz, 6F), -136.5 (dd, $J = 23.5, 7.8$ Hz, 2F), -136.8 (dd, $J = 25.3, 12.3$ Hz, 6F), -151.4 (t, $J = 20.9$ Hz, 1F), -161.4 (td, $J = 22.1, 6.8$ Hz, 2F); ^{13}C NMR (100 MHz; CDCl_3): δ 171.2, 148.2, 147.6, 145.6, 145.1, 120.7, 116.0, 104.6, 103.5, 61.2, 35.4, 29.9, 14.3 ppm; UV-vis (CH_2Cl_2) λ_{max} , nm (log ϵ): 414 (5.69), 507 (4.34), 584 (3.30) nm; fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max} (rel. I): 643, 707 nm (1:2); HR-MS (ESI+, 1% $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$): calculated for $\text{C}_{59}\text{H}_{37}\text{F}_{17}\text{N}_4\text{O}_6\text{S}_3$ $[\text{M}+\text{H}]^+$, 1317.1682, found 1317.1649. **6d**: R_f (silica- $\text{CH}_2\text{Cl}_2/25\%$ hexanes) = 0.20; ^1H NMR (400 MHz; CDCl_3): δ 9.00 (s, 4H), 4.31 (q, $J = 7.1$ Hz, 4H), 4.20 (q, $J = 7.1$ Hz, 1H), 3.55 (t, $J = 7.0$ Hz, 4H), 2.94 (t, $J = 7.0$ Hz, 4H), 1.38 (t, $J = 7.1$ Hz, 6H), 1.30 (t, $J = 7.1$ Hz, 1H), -2.82 (s, 1H) ppm; ^{19}F NMR (376 MHz; CDCl_3): δ -133.6 (dd, $J = 25.3, 12.3$ Hz, 1F), -136.8 (dd, $J = 25.1, 12.2$ Hz, 1F) ppm; ^{13}C NMR (100 MHz; CDCl_3): δ 171.2, 104.5, 61.2, 35.4, 29.9, 14.3 ppm; UV-vis (CH_2Cl_2) λ_{max} , nm (log ϵ): 415 (5.87), 508 (4.59), 583 (3.84); fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max} (rel. I): 645, 707 nm (1:2); HR-MS (ESI+, 1% $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$): calculated for $\text{C}_{64}\text{H}_{46}\text{F}_{16}\text{N}_4\text{O}_8\text{S}_4$ $[\text{M}+\text{H}]^+$, 1431.3100, found 1431.2182.

4.3. 5-(4-[(2-carboxyethyl)thio]-2,3,5,6-tetrafluorophenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (7a)

Prepared as described for the esters **6** from $\text{T}^{\text{F}}\text{PP}$ **5** (100 mg, 10×10^{-6} mol), dissolved in DMF (1 mL), diethylamine (200 μl), and ethyl acetate (4 mL), 3-mercaptopropionic acid (**12**) (10 mg, ~ 1 equivalent) were reacted for 2 h. The crude material was purified by flash chromatography (silica gel–1% $\text{MeOH}/\text{CH}_2\text{Cl}_2$). The reaction with 1 equivalent of **12**, **7a** was

isolated as the major product of the reaction (63 mg, 60%), after the recovery of the low polarity starting material **5H₂** (10% recovery). **7a**; R_f (silica-5% MeOH/CH₂Cl₂) = 0.32; ¹H NMR (400 MHz; CDCl₃): δ 8.93 (s, 4H), 3.62 (s, 1H), 3.06 (s, 1H), 2.88 (s, 1H) ppm; ¹⁹F NMR (376 MHz; CDCl₃): δ -133.73, -133.73, -136.6, -151.4, -161.5; UV-vis (CH₂Cl₂) λ_{max} (log ε): 412 (5.29), 506 (4.15), 583 (3.65) nm; fluorescence emission (λ_{excitation} = λ_{Soret}) (CH₂Cl₂) λ_{max} (rel. I): 642, 707 nm (1:2); HR-MS (ESI+, 100% CH₃CN): calculated for C₄₇H₁₅F₁₉N₄O₂S [M+H]⁺, 1061.0612, found 1061.0619.

5,10,15,20-tetrakis-[4-(2-carboxyethyl)thio-2,3,5,6-tetrafluorophenyl]porphyrin 7d.

Prepared as described for **7a** from T^FPP **5** (50 mg, 51 × 10⁻⁶ mol), dissolved in DMF (0.5 mL), diethylamine (150 μl), and ethyl acetate (3.0 ml), 3-mercaptopropionic acid (**12**) (50 mg, ~10 molar equivalents) were reacted for 4 h. The crude reaction mixture was separated using preparative thin layer plate chromatography (silica-5% CH₃OH/CH₂Cl₂). The tetrasubstituted product **7d** was isolated in 40% as the low polar material next to ~40% of a mixture of tri- and di substituted compounds. **7d**: R_f (silica-10% MeOH/CH₂Cl₂) = 0.35; ¹H NMR (400 MHz; CD₃OD): δ 9.24 (s, 1H), 3.52 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.2 Hz, 1H) ppm; ¹⁹F NMR (376 MHz; CD₃OD): δ -136.1, -140.3 ppm; UV-vis (CH₃OH) λ_{max} (log ε): 409 (5.48), 504 (4.38), 582 (3.85) nm; fluorescence emission (λ_{excitation} = λ_{Soret}) (CH₃OH) λ_{max} (rel. I): 647, 706 nm (1:2); HR-MS (ESI+, 100% CH₃CN): calculated for C₅₆H₃₀F₁₆N₄O₈S₄ [M+H]⁺, 1319.0691, found 1319.0740.

4.4. Reaction of 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (5) with Ethyl 3,4-

Dihydroxybenzoate (**10**).

Reaction conditions adapted from the literature.[43] 5,10,15,20-Tetrakis(pentafluorophenyl)-porphyrin **5** (200 mg, 0.205 mmol) was dissolved in a 50 mL round-bottom flask equipped with a stir bar, reflux condenser, and heating mantle in *N*-methylpyrrolidone (25 mL) and K₂CO₃ (80 mg) was added. Ethyl 3,4-dihydroxybenzoate (**10**) (225 mg, 6 equiv) was added to the mixture. Shielded from light with aluminum foil, the reaction mixture was stirred and heated to 100 °C. Once no further progress of the reaction was detectable by TLC (after ~2 h), CH₂Cl₂ (50 mL) was added to the cooled reaction mixture. After transfer to a separatory funnel, the mixture was extensively washed with distilled water (3 × 100 mL each). The organic layer was isolated, dried (Na₂SO₄), and the solvent was removed by rotary evaporation. A gentle stream of N₂ for several hours ensured that the crude material was thoroughly dried. The crude material was purified by flash chromatography (silica gel–50% CH₂Cl₂/hexanes). The first low polarity fraction was recovered starting material **5H₂** (~ 10 mg, 5% recovery), followed by four major fractions with increasing polarity were isolated to provide, after the removal of the solvents, **8a** (17%), **8b** (presumably as a mixture of the *trans* and *cis*-isomers, 36%), **8c** (21%), and **8d** (4%) as dark purple solids. **8a** as a 2:1 mixture of isomers varying in the position of the ester functionality on the catechol moiety: R_f(silica-CH₂Cl₂/25% hexanes) = 0.89; ¹H NMR (400 MHz, CDCl₃): δ 9.15 (d, *J* = 4.7 Hz, 2H), 9.01 (s, 6H), 7.96 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 2.0 Hz), 7.89 (dd, *J* = 2.0 Hz, 1H), 7.84 (d, *J* = 1.9 Hz), 7.28 (d, *J* = 8.6 Hz), 7.17 (d, *J* = 8.4 Hz, 1H), 4.48 (q, *J* = 6.4 Hz, 2H), 4.43 (dd, *J* = 12.8, 5.6 Hz), 1.49 (t, *J* = 7.2 Hz, 3H), 1.44 (t, *J* = 7.1 Hz, 1H), -2.80 (s, 2H) ppm; ¹⁹F NMR (376 MHz; CDCl₃): δ -136.5 (s, 6F), -136.7 (s, 1F), -139.1 (d, *J* = 23.4 Hz, 1F), -139.5 (d, *J* = 23.3 Hz), -151.4 (s, 3F), -161.4 (s, 6F), -162.1 (dd, *J* = 23.4, 10.3 Hz, 1F) ppm;

^{13}C NMR (100 MHz; CDCl_3): δ 164.9, 147.8, 145.4, 144.2, 141.0, 140.0, 138.9, 136.4, 128.0, 127.4, 118.56, 118.53, 117.1, 115.7, 114.0, 105.0, 103.5, 61.5, 14.33, 14.28 ppm; UV-vis (CH_2Cl_2) λ_{max} (log ϵ): 415 (5.37), 505 (4.25), 585 (3.81) nm; fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max} (rel. I): 641, 708 nm (1:2); HR-MS (ESI+, 1% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$), calculated for $\text{C}_{53}\text{H}_{18}\text{F}_{18}\text{N}_4\text{O}_4$ $[\text{M}+\text{H}]^+$, 1117.1119, found 1117.1121. **8b** as a 2:1 mixture of isomers varying in the position of the ester functionality on the catechol moiety: R_f (silica- CH_2Cl_2 /25% hexanes) = 0.55; ^1H NMR (400 MHz; CDCl_3): δ 9.15 (s, 2H), 8.99 (s, 2H), 7.95 (s, 1H), 7.90 (s), 7.87 (d, 8.3 Hz, 1H) 7.83 (s), 7.28 (s), 7.16 (d, J = 8.4 Hz, 1H), 4.42 (q, 7.1 Hz) 4.45 (q, J = 16.6, 7.9 Hz, 2H), 1.49 (t, J = 7.2 Hz, 3H), 1.44 (t, J = 7.1 Hz, 1H), -2.80 (s, 1H) ppm; ^{19}F NMR (376 MHz; CDCl_3): δ -136.5 (s, 2F), -136.7 (s, 1F), -139.0 (dd, 37.4, 15.8 Hz, 1F), -139.5 (dd, 37.1, 15.3 Hz), -151.5 (t, 20.53 Hz, 1F), -161.5 (s, 2F), -162.2 (td, 21.8, 10.7 Hz, 1F) ppm; ^{13}C NMR (100 MHz; CDCl_3): δ 164.9, 144.2, 143.8, 140.5, 140.0, 128.2, 127.9, 127.4, 127.2, 118.5, 117.1, 104.8, 103.2, 61.5, 14.3 ppm; UV-vis (CH_2Cl_2) λ_{max} (log ϵ): 415 (5.10), 510 (3.91), 585 (3.45) nm; fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max} (rel. I): 643, 707 nm (1:2); HR-MS (ESI+, 1% $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$), calculated for $\text{C}_{62}\text{H}_{26}\text{F}_{16}\text{N}_4\text{O}_8$ $[\text{M}+\text{H}]^+$, 1259.1573, found 1259.1612. **8c** as a 2:1 mixture of isomers varying in the position of the ester functionality on the catechol moiety: R_f (silica- CH_2Cl_2 /25% hexanes) = 0.32; ^1H NMR (400 MHz; CDCl_3): δ 9.17 (s, 6H), 9.01 (d, J = 4.6 Hz, 2H), 7.95 (s, 3H), 7.90 (s), 7.87 (d, 8.0 Hz, 3H), 7.86 (s, 1H), 7.84 (s), 7.26 (d, 8.4 Hz), 7.16 (d, J = 8.4 Hz, 3H), 4.47 (q, J = 7.1 Hz, 6H), 1.47 (q, J = 6.5 Hz, 9H), 1.43 (t, J = 7.1 Hz, 1H), -2.77 (s, 2H) ppm; ^{19}F NMR (376 MHz; CDCl_3): δ -136.4 (2F), -136.6 (3F), -139.0 (3F), -139.4, -151.7 (t, 20.6 Hz, 1F), -161.6 (2F), -162.3 (3F); UV-vis (CH_2Cl_2) λ_{max} (log ϵ): 415 (5.49), 510 (4.40), 585 (3.92) nm; fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max}

(rel. I): 643, 707 nm (1:2); HR-MS (ESI+, 1%CH₂Cl₂/CH₃CN), calculated for C₇₁H₃₄F₁₄N₄O₁₂ [M+H]⁺, 1401.2028, found 1401.2019. **8d** as a 2:1 mixture of isomers varying in the position of the ester functionality on the catechol moiety: R_f (silica-CH₂Cl₂/25% hexanes) = 0.16; ¹H NMR (400 MHz; CDCl₃): δ 9.06 (s, 4H), 7.91 (s, 2H), 7.88 (s), 7.84 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.45 (q, *J* = 7.2 Hz, 4H), 1.47 (t, *J* = 7.1 Hz, 6H), 1.42 (t, *J* = 7.1 Hz, 2H), -2.84 (s, 1H) ppm; ¹⁹F NMR (376 MHz; CDCl₃): δ -136.7 (s, 1F), -139.0 (s, 1F), -139.4 (s), -162.4 (dt, *J* = 20.4, 10.5 Hz, 1F) ppm; UV-vis (CH₂Cl₂) λ_{max} (log ε): 415 (5.31), 510 (4.13), 585 (3.63) nm; fluorescence emission (λ_{excitation} = λ_{Soret}) (CH₂Cl₂) λ_{max} (rel. I): 644, 707 nm (1:2); HR-MS (ESI+, 1%CH₂Cl₂/CH₃CN), calculated for C₈₀H₄₂F₁₂N₄O₁₅ [M+H]⁺, 1542.2404, found 1542.2407.

4.5. Saponification of **8a** and **8d**.

Ethyl ester **8a** or **8d** (10 mg) was dissolved in a 50 mL round-bottom flask equipped with a stir bar, LiOH (20 mg), THF (5.0 ml) and water (5.0 ml). The flask was connected to reflux condenser, shielded from light with aluminum foil, and stirred and heated to reflux. TLC monitored the disappearance of the starting material. Once no further progress of the reaction was detectable (after ~4 h), an acidic buffer (10% NaH₂PO₄ acidified by KHSO₄ until pH 2.5) was added to the crude reaction mixture and the product was extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and removed by rotary evaporation. The crude material was purified via chromatography (silica gel–5% MeOH/CH₂Cl₂) to obtain **9a** or **9d**, respectively, each in ~90% yield (~9.0 mg). **9a**: R_f (silica- 5% MeOH/CH₂Cl₂) = 0.54; ¹H NMR (400 MHz; CD₃OD): δ 9.12 (s, 10H), 7.84 (s, 1H), 7.78 (s, 1H), 7.73 (s, 1H), 7.23 (d, *J* = 8.5 Hz), 7.10 (d, *J* = 8.4 Hz, 1H); ¹⁹F NMR (376 MHz; CD₃OD+CDCl₃): δ -138.9, -141.0, -142.0, -

142.3, -154.3, -159.6, -164.0, -164.6; UV-vis (CH_2Cl_2) λ_{max} , nm (log ϵ): 413 (5.10), 506 (3.95), 583 (3.48); fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_2Cl_2) λ_{max} : 641, 707 nm (1:2); HR-MS (ESI+, 100% CH_3CN): calculated for $\text{C}_{51}\text{H}_{14}\text{F}_{18}\text{N}_4\text{O}_4$ $[\text{M}+\text{H}]^+$, 1089.0728, found 1089.0832. **9d**: R_f (silica- 10% $\text{MeOH}/\text{CH}_2\text{Cl}_2$) = 0.34; ^1H -NMR (400 MHz; CD_3OD): δ 9.24 (s, 3H), 7.83 (s, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.72 (s,), 7.26 (d, J = 8.5 Hz,), 7.14 (d, J = 8.3 Hz, 1H); ^{19}F NMR (376 MHz; $\text{CD}_3\text{OD}+\text{CDCl}_3$): δ -137.8, -140.6, -141.0, -163.6; UV-vis (CH_3OH) λ_{max} , nm (log ϵ): 412 (5.33), 505 (4.13), 581 (3.65); fluorescence emission ($\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$) (CH_3OH) λ_{max} : 643, 707 nm (1:2); HR-MS (ESI+, 100% CH_3CN): calculated for $\text{C}_{76}\text{H}_{42}\text{F}_{12}\text{N}_4\text{O}_{16}$ $[\text{M}+\text{H}]^+$, 1431.1152, found 1431.1230.

Supplementary Data

A reproduction of the full ^1H , ^{19}F , and select ^{13}C NMR, UV-vis, and fluorescence spectra, and CVs of all new compounds reported here.

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Captions

Figure 1. ^1H NMR (400 MHz, CDCl_3 , 25°C) of parent porphyrin **5** and the $\text{T}^{\text{F}}\text{PP}$ mercaptopropionate ester-derivatives **6** indicated.

Figure 2. ^{19}F NMR (376 MHz, CDCl_3 , 25°C) spectra of the parent porphyrin **5** and the $\text{T}^{\text{F}}\text{PP}$ mercaptopropionate ester-derivatives **6** indicated.

Figure 3. ^1H NMR (400 MHz, CDCl_3 , 25°C) spectra of parent porphyrin **5** and the $\text{T}^{\text{F}}\text{PP}$ catechol ester-derivatives **8** indicated.

Figure 4. A. ^{19}F NMR (376 MHz, CDCl_3 , 25°C) spectra of parent porphyrin **5** and the $\text{T}^{\text{F}}\text{PP}$ catechol ester-derivatives **8** indicated.

Figure 5. UV-vis (solid trace) and fluorescence spectra (dotted trace) of the compounds indicated; all in CH_2Cl_2 , $\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$.

Figure 6. Cyclic voltammograms of the compounds indicated. Conditions: 1 mM porphyrin 0.1 M TBAPF₆ in dry CH_2Cl_2 , Pt working and counter electrodes, 200 mV/s scan speed.

Figure 7. Normalized UV-vis spectra of **7a** (top) and **9a** (bottom) in CH_2Cl_2 (solid trace) and adsorbed onto SiO_2 nanoparticles (dotted trace) on an FTO-covered glass slide.

Scheme 1-revised

Scheme 2

Scheme 3

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7