



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.

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1. Introduction

Solid phase-bound porphyrins may find use 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].

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].

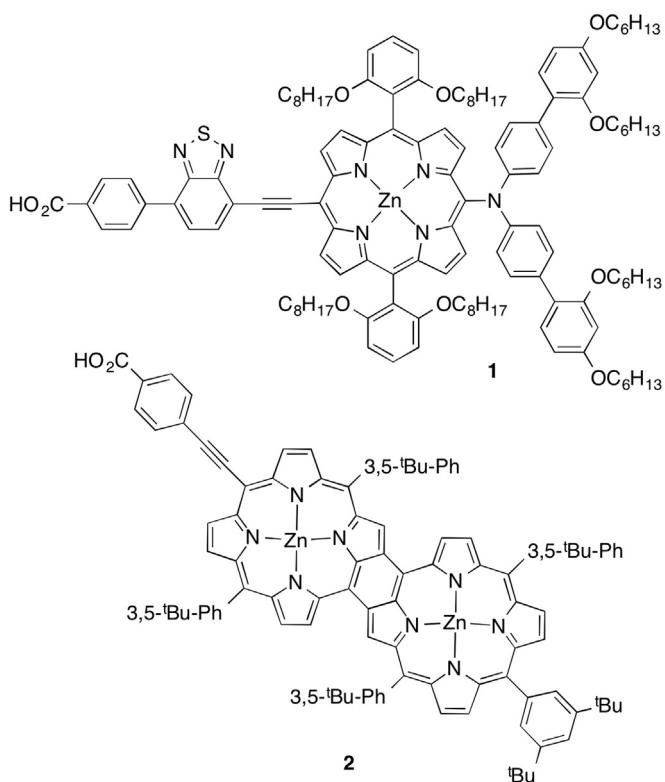
Irrespective of the type of dye, carboxylic acid groups are by far the most common anchoring group for dye attachment to TiO_2 or other metal oxide surfaces [1,4,9,19]. However, from a practical point of view, the synthesis of porphyrinoid dyes with a single or multiple carboxylic acid groups is associated 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 (C_6F_5) groups are particularly appealing in this context [21]. Many *meso*-(C_6F_5)-substituted porphyrinoids are literature-known [21–24], including *N*-fused and confused porphyrin **3** and the porpholactone-based

Abbreviations: DSSC, dye-sensitized solar cell; T^FPP, *meso*-tetrakis(pentafluorophenyl)porphyrin.

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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].

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.

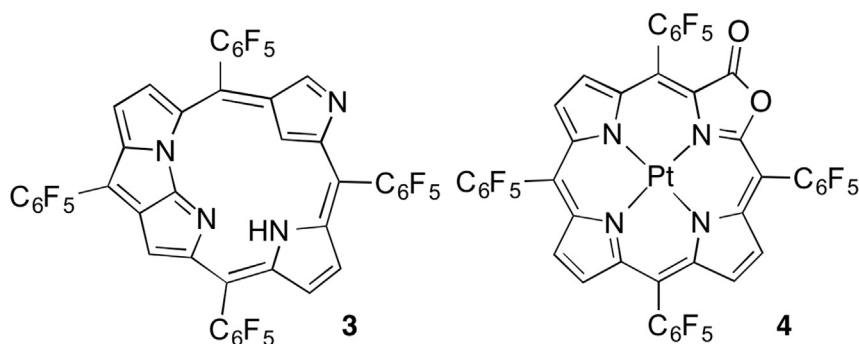
2. Results and discussion

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-

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].

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



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