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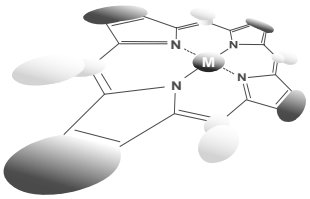

Syntheses and optoelectronic properties of amino/carboxyphenylporphyrins for potential use in dye-sensitized TiO_2 solar cells

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ABSTRACT: New mixed-substituent amino/carboxyphenylporphyrins for a dye-sensitized TiO_2 solar cell were prepared using several synthetic routes. The reaction of 4-carbomethoxy- and 4-acetamidobenzaldehydes with pyrrole in propionic acid under aerobic conditions afforded mixtures of mixed amide/ester substituted tetraphenylporphyrins which were separated using centrifugal chromatography then deprotected to give the target compounds. Condensation of *p*-nitrophenyl-dipyrromethane with 4-carbomethoxybenzaldehyde in CH_2Cl_2 catalyzed by trifluoroacetic acid, followed by oxidation with dichlorodicyanoquinone gives *trans*-dicarbomethoxy/dinitrophenylporphyrin, which when treated with $SnCl_2$ and HCl affords the *trans*-diamino/dicarboxy derivative, *trans*-TA_2C_2PP. Commercially available tetrakis-5,10,15,20-(4-carboxyphenyl)porphyrin (TCPP) was converted to mixtures of mixed amino/carbomethoxyphenylporphyrins using hydroxylamine hydrochloride in polyphosphoric acid with methanol workup. Relative yields and product distributions from each route are discussed and the optoelectronic characteristics of the synthesized porphyrins were studied using UV-visible spectroscopy and cyclic voltammetry.

KEYWORDS: aminophenylporphyrins, carboxyphenylporphyrins, TCPP, TAPP, porphyrin-sensitized solar cells.

INTRODUCTION

The TiO_2 dye-sensitized solar cell (DSSC) first introduced by Grätzel and O'Regan has shown great promise as a simple alternative energy device demonstrating power conversion efficiencies up to 11% under 1 sun irradiation (AM 1.5) using ruthenium photosensitizers [1]. Investigations of tetraphenylporphyrins as the light harvesting dye in TiO_2 DSSCs have also shown promise with efficiencies as high as 4% [2]. In addition to the optimization of porphyrin dyes for DSSCs, research has also focused on developing a solid-state version by replacing the liquid electrolyte with p-type semiconductors [3], polymeric electrolytes [4], amorphous organic hole conductors [5], and conductive polymers such as polythiophenes [6], poly(phenylenevinylenes) [7], and polyanilines [8, 9].

Recently, our lab has reported the feasibility of a porphyrin-polyaniline solid state DSSC with a solar conversion efficiency of 0.8% [10]. This device uses an aniline gel designed for *in-situ* photoelectrochemical generation of polyaniline between the aminophenylporphyrin dye adsorbed on TiO_2 and a polyaniline-coated counter electrode [11]. The porphyrin dye contained three carboxyphenyl

◊SPP full member in good standing

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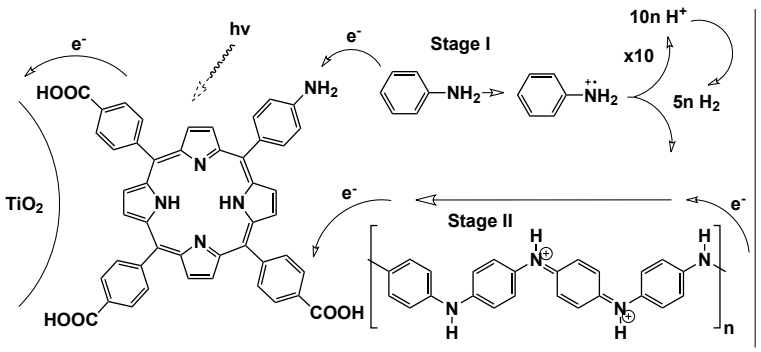
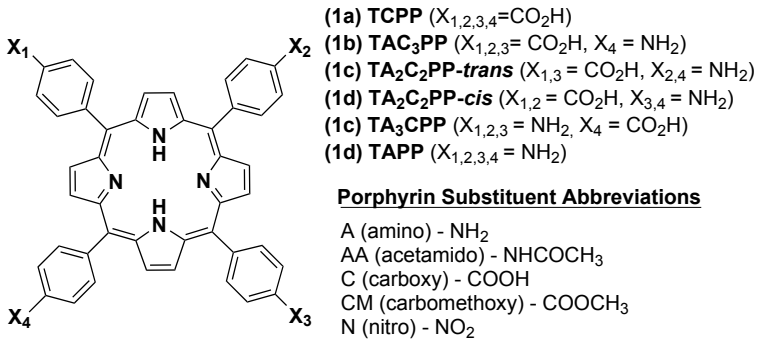


Fig. 1. Photoelectropolymerization of aniline in a porphyrin (5-(4-aminophenyl)-10,15,20-tris(4-carboxyphenyl)porphyrin, TC_3APP) sensitized TiO_2 solar cell [10]



(1a) TCPP ($X_{1,2,3,4}$=CO_2H)
(1b) TAC_3PP ($X_{1,2,3}$= CO_2H, X_4 = NH_2)
(1c) TA_2C_2PP-*trans* ($X_{1,3}$ = CO_2H, $X_{2,4}$ = NH_2)
(1d) TA_2C_2PP-*cis* ($X_{1,2}$ = CO_2H, $X_{3,4}$ = NH_2)
(1c) TA_3CPP ($X_{1,2,3}$ = NH_2, X_4 = CO_2H)
(1d) TAPP ($X_{1,2,3,4}$ = NH_2)

Porphyrin Substituent Abbreviations

A (amino) - NH_2
AA (acetamido) - $NHCOCH_3$
C (carboxy) - COOH
CM (carbomethoxy) - $COOCH_3$
N (nitro) - NO_2

Fig. 2. Tetrakis(4-amino/carboxyphenyl)porphyrin derivatives

substituents to adsorb tightly to the TiO_2 surface, and one aminophenyl group that could chemically bond to the growing polyaniline (Fig. 1).

One goal of this research is to investigate the effect of increasing the number of aminophenyl groups attached to the porphyrin photosensitizer allowing for increased connectivity and charge mobility between the polyaniline phase and the adsorbed porphyrin dye. Therefore, reasonable synthetic access to all four structures of mixed para-amino/carboxyphenyl substituted tetraphenylporphyrins for a polyaniline dye-sensitized TiO_2 solar cell is highly desirable (Fig. 2). In addition, we expect that porphyrin derivatives with both acid and base functionalities may be useful in other optoelectronic applications.

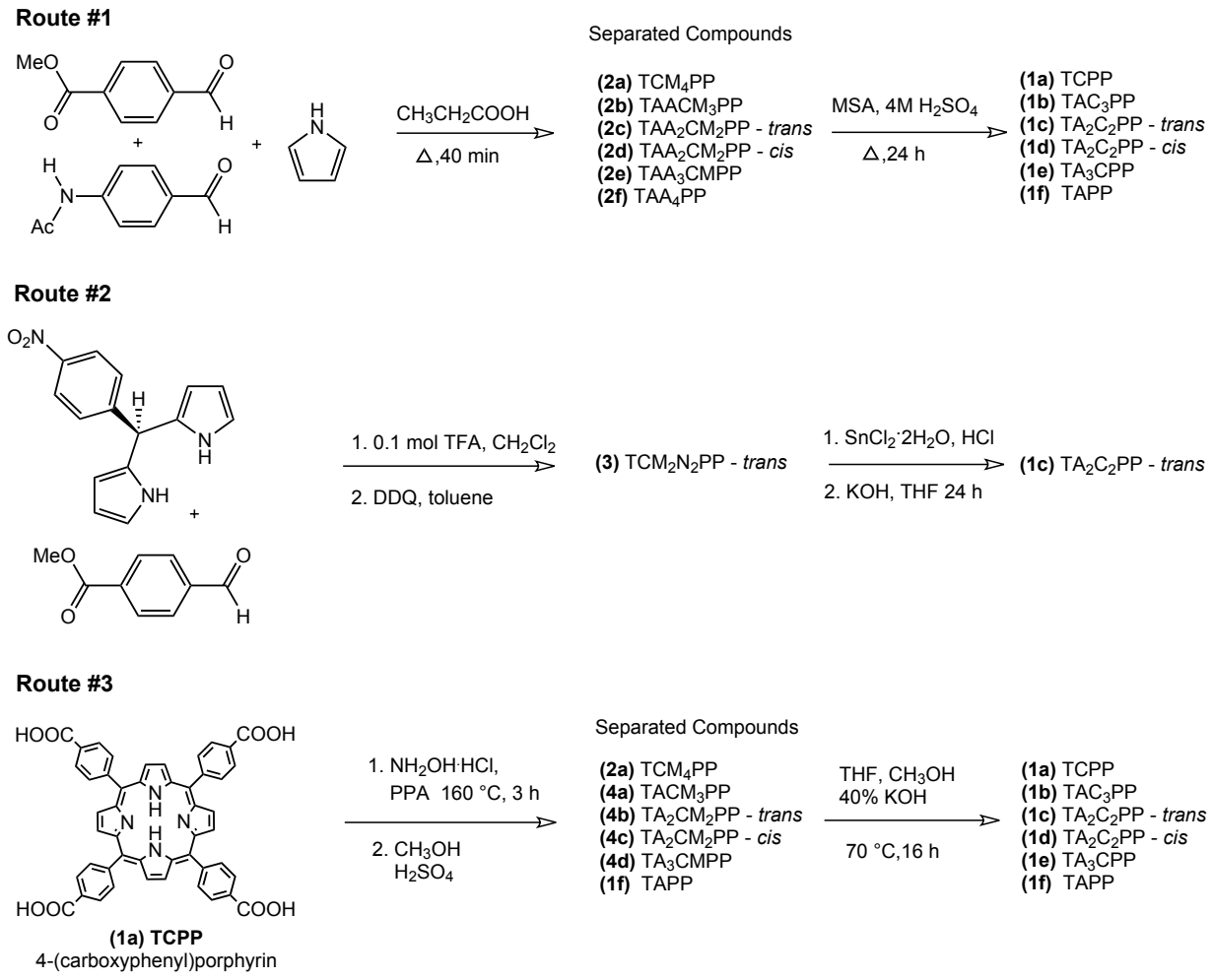
Accessing each of the four target structures (TAC_3PP, *cis*- and *trans*-TA_2C_2PP, TA_3CPP) of mixed amino/carboxy tetraphenylporphyrins is complicated by the acid-base behaviors of the substituents and commonly observed anionic tetraphenylporphyrin aggregation [12]. The protected amino/carboxyphenyl moieties were therefore introduced as acetamido, carbomethoxy, or nitro groups which allowed for clear visualization and separation using standard chromatographic techniques. Three strategies were examined to obtain these new porphyrin derivatives (Scheme 1). The most general method involved refluxing pyrrole and appropriate aromatic aldehydes in propionic acid, modeled after the classic Rothemund [13] and improved Adler/Longo [14] method. This method yields a mixture of six porphyrin products which can be separated using centrifugal chromatographic separation. To obtain exclusively the *trans*-TA_2C_2PP derivative, a [2+2] method [15] was used reacting 4-nitrophenyldipyrromethane and 4-carbomethoxybenzaldehyde under mildly acidic conditions, followed by oxidation with dichlorodicyanoquinone (DDQ) and nitrophenyl reduction to the aminophenyl group using an acidic $SnCl_2$ solution. A third method uses a functional group transformation involving a Lossen rearrangement directly obtaining all the amino/carboxyphenyl porphyrin compounds starting with commercially available tetrakis(4-carboxyphenyl)porphyrin.

This paper details the synthetic methods used to prepare these mixed substituent amino/carboxyphenylporphyrin compounds. We also report the optoelectronic properties of these porphyrins and discuss their suitability as the dye in a solid-state polyaniline/TiO_2 solar cell.

RESULTS AND DISCUSSION

Amide/ester tetraphenylporphyrin synthesis (Route #1)

Using Adler/Longo porphyrin synthesis conditions [14], para-substituted benzaldehydes with acetamido and carbomethoxy protecting groups were reacted with pyrrole in refluxing propionic acid with reagent ratios of 2:1:1 (pyrrole:*p*-acetamidobenzaldehyde: 4-carbomethoxybenzaldehyde) affording a mixture of six porphyrins, each of which was readily visualized on silica TLC. The 2:1:1 reactant ratio gave the highest yield of carboxy/aminophenylporphyrins with an even distribution of the target compounds, approximately 26% TCMPP **(2a)**, 28% $TAACM_3PP$ **(2b)**, 16% *trans*-TAA_2CM_2PP **(2c)**, 21% *cis*-TAA_2CM_2PP **(2d)**, 8% TAA_3CMPP **(2e)**, and 1% TAAPP **(2d)** in the final product mixture. Total yields of mixed porphyrins, as with other syntheses of this type, were low (around 10%); however, a fairly pure, crystalline porphyrin material was collected directly from the reaction mixture using vacuum filtration. Longer crystallization times (24-48 h), in propionic



Scheme 1. Syntheses of amino/carboxyphenylporphyrins

acid, allowed for an increase in the total porphyrin yield (up to 15%). Greater quantities of the tri-and tetra-carbomethoxyporphyrins **(2a, 2b)** were found in the product mixture regardless of starting aldehyde ratios. Favoring the *p*-acetamidobenzaldehyde in the starting reaction mixture decreased the yield of crystallized porphyrin. This is believed to be due to the lower reactivity of *p*-acetamidobenzaldehyde and relatively inefficient crystallization of the *p*-acetamido-containing porphyrins from the propionic acid reaction mixture. Separation of the six statistical products **(2a-f)** was performed using centrifugal chromatography using a 2 mm thick silica plate rotor. Using an acetone and dichloromethane elution scheme, highly colored bands of each porphyrin can be readily visualized and isolated, eluting off the plate in the order **2(a-f)**. The deprotected amino/carboxyphenyl porphyrin analogs were isolated in one step by heating the separated derivatives in methanesulfonic acid and 4M H_2SO_4 for 24 h to ensure complete deprotection of both the acetamido and ester protecting groups.

The *cis*-TAA_2CM_2PP geometry has a more polar molecular configuration causing it to elute off the silica chromatography plate after the *trans*-TAA_2CM_2PP derivative. After separation, the *cis* and *trans* isomers of TAA_2CM_2PP were distinguished using the differences of the beta-pyrrole porphyrin hydrogens noted in the ^1H NMR spectra, although warming the probe to 59 °C was required. Only two types of beta-substituted pyrrole hydrogens are present in the *trans* structure which give rise to two clearly distinguishable doublets (Fig. 3). The *cis* derivative has four different beta-pyrrole hydrogens giving rise to two doublets and two singlets which overlap in the ^1H NMR spectra. These ^1H NMR features can also be observed at room temperature with the *cis* and *trans* TA_2CM_2PP derivatives obtained from Route #3.

[2+2] Porphyrin construction (Route #2)

Direct access to the *trans*-TA_2C_2PP isomer (**1d**) was gained using a [2+2] condensation of a dipyrromethane with an additional aromatic aldehyde in CH_2Cl_2 with trifluoroacetic acid (TFA) as catalyst followed by oxidation with DDQ to the porphyrin structure [16]. Using one of the several methods already reported [17, 18], synthesis of the 4-nitrophenyldipyrromethane was straightforward, yielding

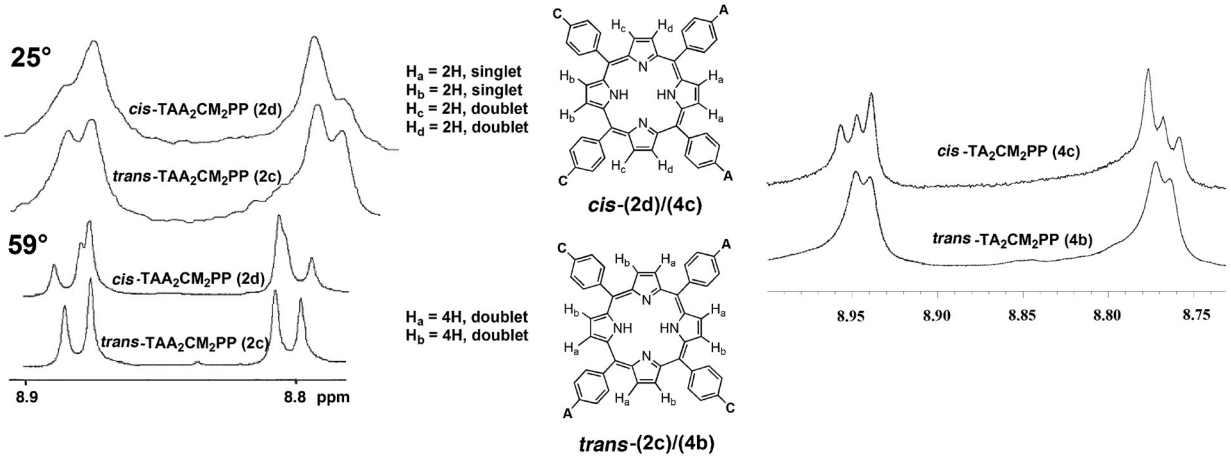


Fig. 3. ^{1}H NMR (500 MHz, d_6-DMSO) of beta pyrrole hydrogen regions for *cis*- and *trans*-TAA_2CM_2PP **(2d, 2c)** derivatives at 25 °C and 59 °C and the ^{1}H NMR (500 MHz, $CDCl_3$) beta pyrrole hydrogen regions for *cis*- and *trans*-TA_2CM_2PP **(4b, 4c)** derivatives at 25 °C

a stable product, which could be purified using standard flash chromatography. It has been noted that dipyrromethanes and tripyrromethanes tend to polymerize slowly upon standing at room temperature [19, 20]. This was observed with acetamidophenyldipyrromethanes that were synthesized but was not observed with the nitrophenyldipyrromethane, which was isolated as bright yellow crystals. The acetamidophenyl derivatives darkened after several days even when kept under vacuum and shielded from light. This has been attributed to the more electron-donating acetamidophenyl functionality which accelerates oxidative polymerization mechanisms [18]. The nitrophenyldipyrromethane was therefore used to obtain the *trans*-TCM_2N_2PP porphyrin following the method of Milanesio *et al*., condensing the nitrophenyldipyrromethane with 4-carbomethoxy benzaldehyde using the mild conditions of dilute TFA in CH_2Cl_2 followed by oxidation with DDQ (yield 21%) [21] (Scheme 1, Route #2).

The method most often used for conversion of tetra(*p*-nitrophenyl)porphyrin (TNPP) to tetra-(p-aminophenyl)porphyrin (TAPP, **1f**), involves warming the nitrophenylporphyrin in a concentrated solution of HCl with $SnCl_2$•$2H_2O$ for 60 min [22, 23]. Using these conditions, the nitro/carbomethoxyphenylporphyrin **(3)** was converted to the amino/carbomethoxyphenylporphyrin derivative **(1c)** in good yields (85%). Typically, the reaction was complete in one hour as monitored by TLC. ^{1}H NMR and mass spectral data indicate that the carbomethoxyphenyl groups remain mostly unaffected by the reaction conditions, although there was some evidence of hydrolysis to free carboxylic acid. The product was warmed in a 40% KOH/THF solution then neutralized to afford the final *trans*-amino/carboxyphenyl porphyrin **(1c)** product with complete ester deprotection.

Carboxy - amino interconversion (Route #3)

A third route directly converts tetra(4-carboxyphenyl)porphyrin, (TCPP, **1a**) into a mixture of the statistical amino/carboxyphenylporphyrin products using a Lossen rearrangement reaction employing hydroxylamine hydrochloride and polyphosphoric acid (PPA) [24]. Complete transformation of TCPP to TAPP can be accomplished using a large excess of hydroxylamine (8:1), while partial transformation with limiting amounts of hydroxylamine (2:1) leads to the full mixture of amino/carboxy derivatives **(1a-f)** in a single reaction. A notable feature of this approach is the statistical favoring of *cis* over *trans* product because of the higher probability (2:1) that the reaction will proceed *cis* to the first substituent that has already been transformed. This feature was evident in the product distribution of reactions when (2:1), (3:1) and (4:1) (hydroxylamine:porphyrin) ratios were used.

Initial conditions for this reaction were studied by completely converting the commercially available tetrakis(4-carboxyphenyl)porphyrin TCPP **(1a)** to TAPP **(1d)** using a large excess of hydroxylamine hydrochloride (8:1). The reaction is performed in one step by heating TCPP with excess hydroxylamine hydrochloride for 3 h in polyphosphoric acid (Scheme 1, Route #3), neutralization with base, and extraction with chloroform to isolate tetrakis(4-aminophenyl)porphyrin TAPP in good yield (80%). By diminishing the molar ratio of hydroxylamine hydrochloride to TCPP from 8:1 to 2:1, mixtures of all of the amino/carboxyphenylporphyrins could be acquired in high yields (96%) (see the MALDI-TOF analysis – Fig. 4). Using a 2:1 mole ratio of hydroxylamine to TCPP, the observed porphyrin distribution in the product mixture was approximately 3% TCPP **(2a)**, 13% TAC_3PP **(2b)**, 12% *trans*-TA_2C_2PP **(2c)**, 36% *cis*-TA_2C_2PP **(2d)**, 27% TA_3CPP **(2e)**, and 9% TAPP **(2d)**.

Molar ratios of 4:1 yielded a product distribution which favored TAPP **(1f)** and TCA_3PP **(1e)** formation and was approximately 1% TCPP **(2a)**, 3% TAC_3PP **(2b)**, 8% *trans*-TA_2C_2PP **(2c)**, 22% *cis*-TA_2C_2PP **(2d)**, 33% TA_3CPP **(2e)**, and 33% TAPP **(2d)**. These distributions were determined from isolated weights after preparative TLC.

It was necessary to heat the mixture overnight with distilled water (20 mL) added to the reaction mixture to ensure complete hydrolysis of amide bonds formed between the carboxy and amino substituents. However, the mixtures of the free carboxy and amine-containing porphyrins **(1a-f)** could not be effectively separated using centrifugal chromatography or reverse phase C-18 silica. Therefore, after the intial reaction was complete, the workup procedure was modified using MeOH/conc. H_2SO_4 (80 mL/10 mL) added to the PPA/porphyrin mixture and heated (60 °C) to form the methyl ester derivatives. After neutralizing the solution with dilute NH_4OH to a pH of 7, the derivatives were readily extracted into chloroform and successfully separated using preparative thin layer chromatography. The overall method is a remarkably direct approach to the amino/carbomethoxyphenylporphyrins; however the final isolation requires an additional methyl ester deprotection step after chromatographic separation to afford the target compounds.

Synthetic route comparisons

Each of the three methods examined show some synthetic advantages for the synthesis of amino/carboxyphenylporphyrins. Table 1 summarizes the product distribution and yields for the various routes studied. The classic Adler-Longo method is the most straightforward route using simple starting materials with protected functional groups that allow for clear band separation and visualization on a centrifugal chromatography plate. Starting reactant ratios of 2:1:1 (pyrrole:*p*-acetamidobenzaldehyde:4-carbomethoxybenzaldehyde) were used and gave preference to the *cis*/*trans* and tricarbomethoxy derivatives. This represented both the higher reactivity of the carbomethoxybenzaldehyde and the favored crystallization of the carbomethoxy containing porphyrins. A drawback to this method is the low initial mixture yield (10%) and the centrifugal chromatographic separation limited to 20-40 mg of porphyrin mixture per separation.

The second method provides a direct route to *trans*-TA_2C_2PP using a [2+2] dipyrromethane/aldehyde reaction which consistently provided good yields. Preparation of the 4-nitrophenyldipyrromethane precursor is straightforward, requiring little purification. Yields of the single nitro/carboxyphenylporphyrin macrocycle are good (21%). This method is contingent upon a final nitro group reduction which shows some loss of porphyrin product (yield 85%); however the reaction can be completed in ambient conditions with minimal workup [24]. It is tempting to apply a similar stepwise methodology to gain access to the other target porphyrin derivatives (*cis*-TA_2C_2PP, TA_3CPP, and TAC_3PP). Unfortunately, the available methods to synthesize multifunctional porphyrins were reported to be incompatible with amide functionalities and would be incompatible with a nitrophenyl functionality, (Rao *et al.* - dipyrromethane monoacylation using EtMgBr) [25].

The final method offers a novel tetraphenylporphyrin substituent transformation starting with commercially available tetrakis(4-carboxyphenyl)-porphyrin. This method gives high yields (> 98%) using straightforward synthetic techniques and chromatographic separations. The product distribution from the 2:1 synthesis shows good yields of the *cis*/*trans* and tricarbomethoxy derivatives and allowed for a much higher yield of the triaminophenylporphyrin which was not readily available using Route #1. Of

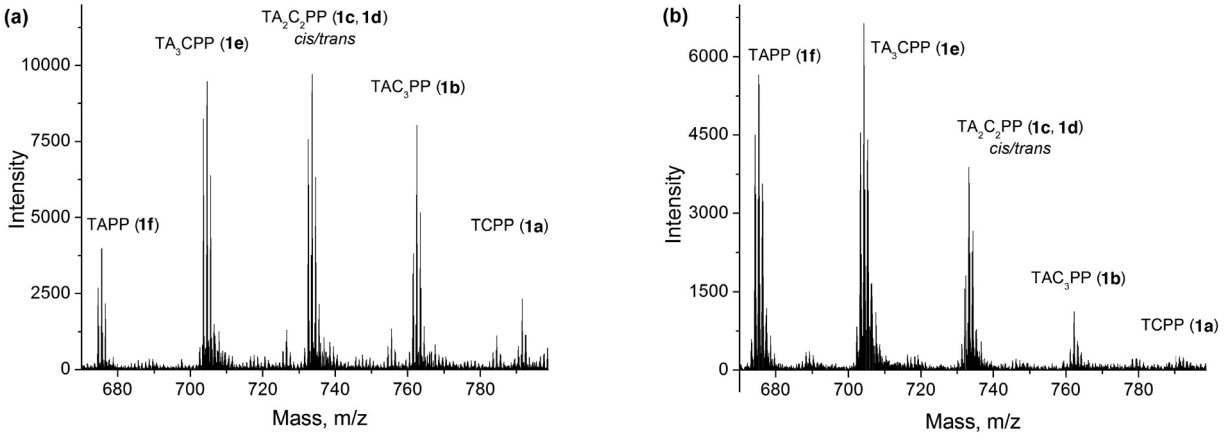


Fig. 4. MALDI-TOF spectra for product mixtures **(1a-f)** from Route #3, heating **(a)** (2 :1) hydroxylamine hydrochloride: tetrakis(4-carboxyphenyl)porphyrin and **(b)** (4:1) in polyphosphoric acid for 3 h

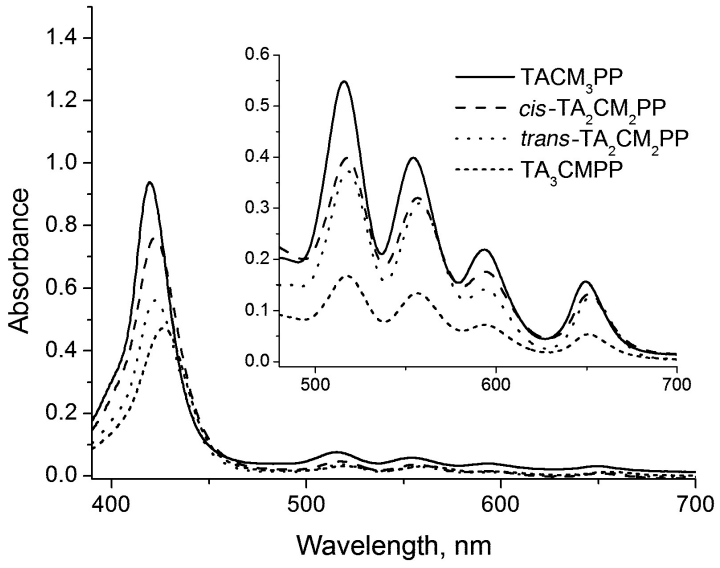


Fig. 5. UV-visible spectra of amino/ester porphyrin derivatives **(4a-d)** in THF (70 μM) using a 0.1 cm cuvette. Inset: Q-band region (480-700 nm) using a 1 cm cuvette

Table 1. Summary of synthetic Routes #1, #2, and #3 and carboxy/aminophenylporphyrin product distribution

Method	Overall Yield	Separation Method	Products, Distribution
Route 1 *pyrrole + benzaldehydes*	10%	centrifugal chromatography	**2b** 28% **2c** 16% **2d** 21% **2e** 8%
Route 2 *dipyrromethane + carbomethoxy benzaldehyd*e	18%	column chromatography	**4b** 100%
Route 3 *TCPP (1a) + hydroxylamine*	96%	preparative TLC	**4a** 13% **4b** 12% **4c** 36% **4d** 27%

the two mixed substituent methods studied, we found this to be a superior method due to the convenience of a commerically available starting porphyrin and the avoidance of isolating crystallized porphyrin compounds from a crude reaction mixture.

Spectroscopic characterizations

Tetraphenylporphyrins are well-suited for dye-sensitized photovoltaic cells with a high molar extinction coefficient at the Soret band (420-430 nm) in the order of ε = 400000 $M^{-1}.cm^{-1}$ with additional Q band absorptions extending out to 650 nm [26]. The Q(*IV*) absorbance for TCPP **(1a)** (ε = 26000 $M^{-1}.cm^{-1}$, λ = 512 nm) is more intense than the more popular DSSC ruthenium sensitizers (*e.g.*, N-719, ε = 13600 M^{-1}-cm^{-1}, λ_{max} = 535 nm) although the latter shows a slightly broader absorbance further out into the visible region [1]. The four target amino/carboxyphenylporphyrin compounds contain unique arrangements of both electron-donating and electron-withdrawing moieties. Typically, electron-donating meso-substituents cause red shifts for both the Soret (B) and Q bands. The magnitude of these shifts in meso-substituted tetraphenylporphyrins has previously been correlated with Hammett substituent constants [27].

The UV-vis spectra of the four amino/carbomethoxyphenyl porphyrin compounds **(4a-d)** show a decreasing molar absorptivity and red-shifted peaks with increasing numbers of aminophenyl substituents (Fig. 5). The same trends are observed for the amino/carboxyphenyl porphyrins (**1b-e**), *e.g.* the Soret band absorbance shifts from 416 nm for compound **1b** to 427 nm for **1e** in THF. Although the molar absorptivity decreases with increasing aminophenyl substituents, the peaks are significantly broadened and the molar extinction coefficients are still relatively high (*cis*-TA_2C_2PP, ε = 25300 $M^{-1}.cm^{-1}$, 427 nm and ε = 1600 $M^{-1}.cm^{-1}$, λ = 523 nm) which make these compounds good candidates for sensitizing TiO_2 in a dye-sensitized solar cell.

Absorbance variations between the *cis* and *trans* TA_2CM_2PP porphyrins were also observed with increased and slightly red-shifted absorbance of the *cis*-TA_2CM_2PP derivative. These variations are attributed to the decreased symmetry of the *cis*-TA_2CM_2PP derivative giving rise to intramolecular charge-transfer character in π-π* absorption bands. This effect has been noted before with *cis* and *trans* nitro/aminophenyl porphyrin derivatives that were synthesized and studied as "push-pull" porphyrins [28]. The overall magnitude of the intramolecular electron transfer character for tetraphenylporphyrins containing electron donating and withdrawing substituents was found to be minimal, attributed to decreased π electron overlap due to the dihedral angle of the meso-substituted phenyl groups which are twisted from the plane (~60°) of the porphyrin macrocycle [29].

Electrochemical characterizations

For efficient light harvesting and TiO_2 sensitization in a DSSC, the dye's LUMO level must be situated above the conduction band of the TiO_2 nano-particulate layer thereby providing a thermodynamic driving force for light-induced charge separation [30]. In addition, the HOMO level of the dye must be

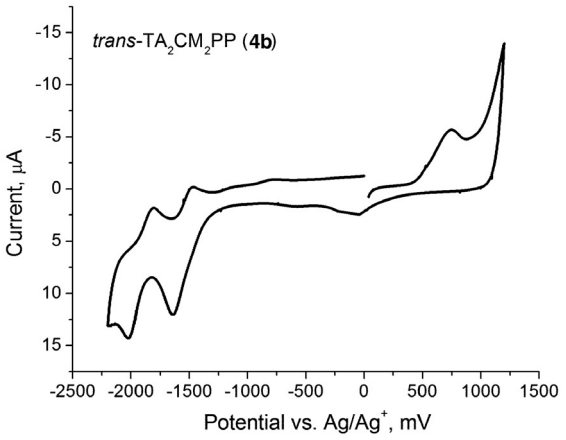


Fig. 6. Cyclic voltammogram of *trans*-TA_2CM_2PP **(4b)** in deaerated (Ar) dichloromethane (1 mM) solution with TBAP (tetra-*n*-butylammonium perchlorate) supporting electrolyte measured with a with glassy carbon electrode cycling at 50 $mV.s^{-1}$

situated below that of the electron donor, such as the aniline monomer used for the photoelectrochemical growth of polyaniline [10]. The open circuit voltage of the cell is determined using the difference between the quasi-Fermi level of the TiO_2 under illumination (4.2 eV) and the redox potential of the hole conductor polyaniline and is theoretically not contingent on the band gap of the porphyrin dye [31].

For reversible redox reactions, cyclic voltammetry can give a direct measure of the HOMO and LUMO levels. Since these porphyrins generally exhibited irreversible redox behavior, the values obtained can only be considered approximations to the relevant energy levels. The amino/ester porphyrins were readily soluble in dichloromethane and cyclic voltammetry was conducted as described earlier [32]. (Fig. 6) Although the eventual porphyrin dye will bear free carboxylic acid groups for binding onto the TiO_2 surface, the difference between measured redox potentials for tetrakis(4-carboxyphenyl)porphyrin and tetrakis(4-carbomethoxyphenyl)porphyrin is minimal [32]. The $E_{1/2}$ values (Table 2) were translated into electrochemical ionization and electron affinity potentials in eV [33] and matched with literature values obtained for polyaniline [34], TiO_2, and TAPP/TCMPP parent compounds [32] to create a potential energy diagram for the solar cell (Fig. 7).

The gradual energy level trends match well with the redox differences between the parent compounds, TAPP and TCMPP. In addition, the band gap decreases slightly with increasing numbers of aminophenyl

Table 2. Measured redox potentials *vs*. $Ag/AgNO_3$ for amino/ester porphyrin derivatives **(4a-d)**

Compound	E_{ox} (V)	E^1_{red} (V)	E^2_{red} (V)
$TACM_3PP$ **(4a)**	0.85	-1.50	-1.81
TA_2CM_2PP **(4b)** *trans*	0.75	-1.56	-1.92
TA_2CM_2PP **(4c)** *cis*	0.74	-1.48	-1.82
TA_3CMPP **(4d)**	0.37	-1.59	-1.92

groups which is in agreement with the red-shifted absorbance spectra observed among the porphyrin derivatives. Both TA_3CMPP and *trans*-TA_2CM_2PP exhibited electrode film formation upon repeated scanning in dichloromethane. It has been shown that dichloromethane is an excellent solvent system for the electropolymerization of TAPP [35]. Interestingly, the *cis*-TA_2CM_2PP derivative showed little or no deposited film after successive cycling.

For the polyaniline/porphyrin/TiO_2 cell to operate efficiently, an initial polyaniline growth step is required. This step requires oxidation of the aniline monomer by the porphyrin dye. The HOMO level of the dye should therefore be lower than that of the aniline monomer for efficient electrochemical oxidation allowing for the initiation of the aniline polymerization. By measuring the growth of the photocurrent generated under illumination, it was demonstrated that this polyaniline growth process does occur in a DSSC sensitized with the TAC_3PP **(1b)** porphyrin derivative [10]. All of the porphyrin dyes reported here show HOMO/LUMO levels comparable to TAC_3PP **(1b)** which match appropriately to both the TiO_2 and the polyaniline energy levels.

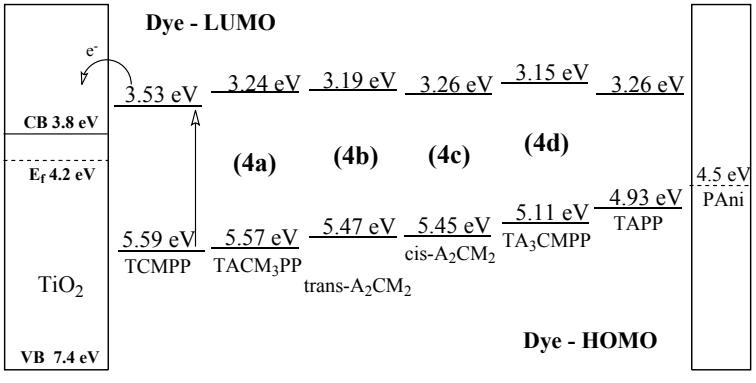


Fig. 7. Energy level (eV) comparison for porphyrins **4a-d** including TCMPP and TAPP [22] and the TiO_2/polyaniline [23] components of the solid-state porphyrin-sensitized solar cell

EXPERIMENTAL

General

Tetrakis(4-aminophenyl)porphyrin (TAPP) and tetrakis(4-carboxyphenyl)porphyrin (TCPP) used for synthesis, spectroscopy, and electrochemistry were obtained and used as received from TCI America (Portland, OR). Solvents were purchased as reagent or spectroscopic grade and used as received. Centrifugal chromatography was performed on a Chromatotron (Model 7924T – Harrison Research, Inc.) using a 2 mm thick silica plate, which was prepared using TLC grade silica (Aldrich). Column chromatography was performed using 60-200 mesh silica gel purchased from Aldrich. Thin layer chromatography was conducted using silica TLC plates with fluorescent indicator (Fisher). Redox potentials were measured using three-probe cyclic voltammetry with a Princeton Applied Research Model 263 potentiostat using Win-EChem processing software, a glassy carbon working electrode (0.35 cm^2), and a coiled platinum wire counter electrode. Porphyrin redox potentials were determined in argon-degassed dichloromethane solutions (0.01 M porphyrin concentration) with 0.1 M TBAP (tetra-*n*-butylammonium perchlorate) supporting electrolyte. Scan ranges were +1.20 V to -2.20 V *vs*. $Ag/AgNO_3$ reference electrode using a 50 $mV.s^{-1}$ scan rate. UV-vis spectra (λ_{max} in nm, ε in $M^{-1}.cm^{-1}$) were obtained with a Shimadzu Model 260 UV-Visible spectrometer using 0.8 mm slit widths. NMR spectra were acquired on GE 500 (500 MHz) NMR with TMS as reference (δ in ppm, *J* in Hz). Mass spectra (MALDI-TOF) were obtained at the Laboratory for Bioanalysis and Biotechnology at Washington State University and the Bio-Analytical Shared Resource/Pharmacokinetics Core at the Oregon Health & Science University.

Synthesis

Preparation of mixed substituent porphyrins (2b-e) and (1b-e) - Route #1, Scheme 1

A solution of 4-acetamidobenzaldehyde (11.55 g, 70.8 mmol) and 4-carbomethoxybenzaldehyde (11.62 g, 70.8 mmol) in propionic acid (225 mL) was heated to reflux for 5 min followed by slow addition of pyrrole (9.51 g, 141.6 mmol) over 15 min. After heating at reflux for an additional 40 min and cooling to room temperature, the reaction solution was filtered to yield a crystallized porphyrin material (~ 0.1 g), which was rinsed with ice-cold methanol. The heavy tars at the bottom of the flask were discarded, and the filtrate was allowed to sit for several days at room temperature which, after successive filtrations, yielded a larger quantity of the porphyrin mix (1.4 g, 10% yield). Silica TLC (10% CH_3OH:$CHCl_3$) indicated six porphyrin products (R_f: **2a** = 0.89, **2b** = 0.50, **2c** = 0.40, **2d** = 0.33, **2e** = 0.23, **2f** = 0.11). Separation of the mix was performed by applying the porphyrin mixture to a silica centrifugal chromatography plate (2 mm thick, Chromatotron), and eluting with a gradient of CH_2Cl_2 and acetone, (from 20:1 to 1:1 using 50 mL per gradient). The six derivatives eluted in the order **2a-f**.

5-(4-Acetamidophenyl)-10,15,20-tris(4-carbomethoxyphenyl)porphyrin (TAACM$_3$PP, 2b). Using centrifugal chromatography, the **2a-f** mixture (0.02 g in 1 mL $CHCl_3$) was applied and eluted with (15:1) CH_2Cl_2:acetone (50 mL); collecting the second band gave TAACM$_3$PP, 0.006 g (28% of the original mix). UV-vis (THF): λ_{max}, nm (log ε) 419 (5.49), 515 (4.18), 549 (3.90), 591 (3.65), 647 (3.53). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.94 (2H, s, pyrrole-NH), 2.23 (3H, s, -NHCOC*H$_3$*), 4.05 (9H, s, -CO_2CH_3), 8.06 (2H, d, *J* = 8.7, Ph-acetamido), 8.15 (2H, d, *J* = 8.5, Ph-acetamido), 8.37 (6H, m, Ph-carbomethoxy), 8.41 (6H, m, Ph-carbomethoxy), 8.83 (6H, bs, pyrrole-H), 8.91 (2H, bs, pyrrole-H), 10.43 (1H, s, -NHCOMe). MS (MALDI-TOF): *m/z* 845.53. Calcd. for [$C_{52}H_{39}N_5O_7$] 845.28.

5,15-Di(4-acetamidophenyl)-10,20-di(4-carbomethoxyphenyl)porphyrin (*trans*-TAA2C$_M$2P$_P$, 2c). Using centrifugal chromatography, eluting with (12:1) CH_2Cl_2:acetone (50 mL) and collecting the third band gave *trans*-TAA_2CM_2PP, 0.003 g (16% of the original mix). UV-vis (THF): λ_{max}, nm (log ε) 420 (5.39), 515 (4.00), 551 (3.81), 593 (3.49), 650 (3.48). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm –2.81 (2H, s, pyrrole-NH), 2.36 (6H, s, -NHCOC*H$_3$*), 4.11 (6H, s, -CO_2CH_3), 7.63 (2H, s, -NHCO-), 7.90 (4H, d, *J* = 7.9, Ph-acetamido), 8.15 (4H, d, *J* = 7.9, Ph-acetamido), 8.24 (4H, d, *J* = 7.9, Ph-carbomethoxy), 8.41 (4H, d, *J* = 7.9, Ph-carbomethoxy), 8.76 (4H, d, *J* = 3.9, pyrrole-H), 8.87 (4H, d, *J* = 3.9, pyrrole-H). MS (MALDI-TOF): *m/z* 844.64. Calcd. for [$C_{52}H_{40}N_6O_6$] 844.30.

5,10-Di(4-acetamidophenyl)-15,20-di(4-carbomethoxyphenyl)porphyrin (*cis*-TAA$_2$CM$_2$PP, 2d). Using centrifugal chromatography, eluting with (10:1) CH_2Cl_2:acetone (50 mL) and collecting the fourth band gave *cis*-TAA_2CM_2PP, 0.004 g (21% of the original mix). UV-vis (THF): λ_{max}, nm (log ε) 420 (5.36), 515 (3.98), 551 (3.77), 591 (3.48), 648 (3.41). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.92 (2H, s, pyrrole-NH), 2.22 (6H, s, -NHCOC*H$_3$*), 4.05 (6H, s, -CO_2CH_3), 8.05 (4H, d, *J* = 8.5, Ph-acetamido), 8.14 (4H, d, *J* = 8.5, Ph-acetamido), 8.37 (4H, d, *J* = 8.4, Ph-carbomethoxy), 8.41 (4H, d, *J* = 8.4, Ph-carbomethoxy), 8.82 (4H, bs, pyrrole-H), 8.90 (4H, bs, pyrrole-H), 10.41 (2H, s, -NHCO-). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si, 59 °C): δ_H, ppm –2.84 (2H, s, pyrrole-NH), 2.22 (6H, s, -NHCOC*H$_3$*), 4.05 (6H, s, -CO_2CH_3), 8.03 (4H, d, *J* = 8.5, Ph-

acetamido), 8.12 (4H, d, *J* = 8.5, Ph-acetamido), 8.35 (4H, d, *J* = 8.4, Ph-carbomethoxy), 8.40 (4H, d, *J* = 8.4, Ph-carbomethoxy), 8.80 (4H, m, pyrrole-H), 8.87 (2H, s, pyrrole-H), 8.88 (2H, d, *J* = 4.9, pyrrole-H), 10.25 (2H, s, -NHCO-). MS (MALDI-TOF): *m/z* 844.09. Calcd. for [$C_{52}H_{40}N_6O_6$] 844.30.

5,10,15-Tris(4-acetamidophenyl)-20-(4-carbomethoxyphenyl)porphyrin (TAA$_3$CMPP, 2e). Using centrifugal chromatography, eluting with (8:1) CH_2Cl_2:acetone (50 mL) and collecting the fifth band gave TAA$_3$CMPP, 0.002 g (8% of the original mix). UV-vis (THF): λ_{max}, nm (log ε) 424 (5.11), 516 (3.61), 555 (3.69), 597 (3.40), 649 (3.08). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.9 (2H, s, pyrrole-NH), 2.23 (9H, s, -NHCOC*H$_3$*), 4.05 (3H, s, -CO_2CH_3), 8.06 (6H, d, *J* = 8.3, Ph-acetamido), 8.14 (6H, d, *J* = 8.3, Ph-acetamido), 8.37 (2H, d, *J* = 8.5, Ph-carbomethoxy), 8.41 (2H, d, *J* = 8.5, Ph-carbomethoxy), 8.81 (2H, bs, pyrrole-H), 8.88 (6H, bs, pyrrole-H), 10.39 (3H, s, -NHCO-). MS (MALDI-TOF): *m/z* 843.44. Calcd. for [$C_{52}H_{41}N_7O_5$] 843.32.

5-(4-Aminophenyl)-10,15,20-tris(4-carboxyphenyl)porphyrin (TAC$_3$PP, 1b). A sample of **2b** (0.02 g, 0.024 mmol) was dissolved in methanesulfonic acid (5 mL) and 4M H_2SO_4 (8 mL). The solution was heated to reflux for 60 h, allowed to cool, and the pH was adjusted to 5.5 - 5.7 using 1M NaOH. The solution was extracted with ethyl acetate, dried over Na_2SO_4, and evaporated to dryness to afford 0.015 g (83%) of a dark purple solid (TAC$_3$PP). UV-vis (EtOH): λ_{max}, nm (log ε) 416 (5.40), 514 (4.14), 550 (3.95), 590 (3.72), 647 (3.63). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.86 (2H, s, pyrrole-NH), 7.02 (2H, d, *J* = 8.3, Ph-amino), 7.88 (2H, d, *J* = 8.3, Ph-amino), 8.35 (6H, d, *J* = 8.1, Ph-carboxy), 8.39 (6H, d, *J* = 8.1, Ph-carboxy), 8.83 (6H, s, pyrrole-H), 9.00 (2H, d, *J* = 3.5, pyrrole-H), 13.02 (3H, bs, -COOH). MS (MALDI-TOF): *m/z* 761.21. Calcd. for [$C_{47}H_{31}N_5O_6$] 761.23.

5,15-Di(4-aminophenyl)-10,20-di(4-carboxyphenyl)porphyrin (*trans*-TA$_2$C$_2$PP, 1c). A sample of **2c** (0.02 g, 0.024 mmol) was treated as above to afford 0.010 g, 58% of a purple solid (*trans*-TA$_2$C$_2$PP). UV-vis (DMSO): λ_{max}, nm (log ε) 423 (5.00), 520 (3.83), 564 (3.81), 655 (3.54). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.78 (2H, s, pyrrole-NH), 7.07 (4H, d, *J* = 8.2, Ph-amino), 7.92 (4H, d, *J* = 8.2, Ph-amino), 8.40 (4H, d, *J* = 8.1, Ph-carboxy), 8.45 (4H, d, *J* = 8.1, Ph-carboxy), 8.85 (4H, d, *J* = 4.1, pyrrole-H), 9.02 (4H, d, *J* = 4.1, pyrrole-H). MS (MALDI-TOF): *m/z* 732.13. Calcd. for [$C_{46}H_{32}N_6O_4$] 732.25.

5,10-Di(4-aminophenyl)-15,20-di(4-carboxyphenyl)porphyrin (*cis*-TA$_2$C$_2$PP, 1d). A sample of **2d** (0.02 g, 0.024 mmol) was treated as above to afford 0.012 g, 69% of a light purple solid (*cis*-TA$_2$C$_2$PP). UV-vis (DMSO): λ_{max}, nm (log ε) 427 (4.40), 523 (3.20), 570 (3.36), 661 (3.04). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.79 (2H, s, pyrrole-NH), 7.02 (4H, d, *J* = 8.3, Ph-amino), 7.87 (4H, d, *J* = 8.3, Ph-amino), 8.33 (4H, d, *J* = 8.2, Ph-carboxy), 8.39 (4H, d, *J* = 8.1, Ph-carboxy), 8.78 (2H, d, *J* = 4.5, pyrrole-H), 8.80 (2H, s, pyrrole-H), 8.95 (2H, s, pyrrole-H), 8.97 (2H, d, *J* = 4.5, pyrrole-H). MS (MALDI-TOF): *m/z* 732.21. Calcd. for [$C_{46}H_{32}N_6O_4$] 732.25.

5,10,15-Tris(4-aminophenyl)-20-(4-carboxyphenyl)porphyrin (TA$_3$CPP, 1e). A sample of **2e** (0.015 g, 0.024 mmol) was treated as above to afford 0.01 g, 80% of a purple solid (TA$_3$CPP). UV-vis (DMSO): λ_{max}, nm (log ε) 429 (4.63), 523 (3.11), 571 (3.26), 660 (3.00). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.77 (2H, s, pyrrole-NH), 7.00 (6H, d, *J* = 8.3, Ph-amino), 7.86 (6H, d, *J* = 8.2, Ph-amino), 8.33 (2H, d, *J* = 7.8, Ph-carboxy), 8.38 (2H, d, *J* = 7.8, Ph-carboxy), 8.76 (2H, bs, pyrrole-H), 8.9 (6H, s, pyrrole-H); MS (MALDI-TOF): *m/z* 703.23. Calcd. For [$C_{45}H_{33}N_7O_2$] 703.27.

[2+2] Synthesis of 3 and 1c – Route #2, Scheme 1

5,15-Di(4-carbomethoxyphenyl)-10,20-di(4-nitrophenyl)porphyrin (*trans*-TCM$_2$N$_2$PP, 3). A sample of **3** was obtained as described in the literature [21] from the reaction of 4-carbomethoxybenzaldehyde (0.635 g, 3.87 mmol) with *bis*-4-nitrophenyldipyrro methane (1.03 g, 3.87 mmol) [17] which afforded a purple solid (0.3 g, 21%). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm –2.83 (2H, s, pyrrole-NH), 4.12 (6H, s, -CO_2CH_3), 8.30 (4H, d, *J* = 8.2, Ph-nitro), 8.40 (4H, d, *J* = 8.6, Ph-carbomethoxy), 8.47 (4H, d, *J* = 8.2, Ph-nitro), 8.66 (4H, d, J = 8.6, Ph-carbomethoxy), 8.79 (4H, d, *J* = 4.4, pyrrole-H), 8.86 (4H, d, *J* = 4.4, pyrrole-H). MS (ES): *m/z* 821.45 ([M + H]$^+$ calcd. for [$C_{48}H_{33}N_6O_8$] 821.81).

5,15-Di(4-aminophenyl)-10,20-di(4-carboxyphenyl)porphyrin (*trans*-TA$_2$C$_2$PP, 1c). A sample of **3** (0.1 g, 0.07 mmol) was dissolved in 37% HCl (20 mL). To this solution was added $SnCl_2 \cdot 2H_2O$ (0.6 g, 0.2 mmol), and the reaction mixture was heated at 65 ºC for 60 min. The mixture was quenched with NH_4OH to a pH of 5.5 and extracted with $CHCl_3$. After drying and evaporation of the solvent, the purple solid was hydrolyzed in a solution of THF/CH_3OH (2:1) (27 mL) and 40% KOH (5.4 mL). The mixture was stirred under argon for 16 h, 70 ºC, cooled to room temperature, and adjusted to a pH of 5.8 using concentrated HCl and 1M HCl. The solution was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and evaporated to dryness, affording a purple solid (0.076 g, 85%). The product matches **1c** obtained from the previous amide/ester route (Route #1). ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.78 (2H, s, pyrrole-NH), 7.06 (4H, d, *J* = 8.2, Ph-amino), 7.91 (4H, d, *J* = 8.2, Ph-amino), 8.40 (4H,

d, *J* = 8.1, Ph-carboxy), 8.45 (4H, d, *J* = 8.1, Ph-carboxy), 8.85 (4H, d, *J* = 4.1, pyrrole-H), 9.02 (4H, d, *J* = 4.1, pyrrole-H). MS (ES): *m/z* 733.47 ($[M + H]^+$ calcd. for $[C_{46}H_{33}N_6O_4]$ 733.25).

TCPP (1a) conversion to TAPP (1f) and mixed substituent porphyrins (4a-d) – Route #3, Scheme 1

Tetrakis(4-aminophenyl)porphyrin (1f). Tetrakis(4-carboxyphenyl)porphyrin **(1a)** (0.05 g, 0.063 mmol), an 8:1 excess of NH_2OH•HCl (0.035 g, 0.503 mmol), and polyphosphoric acid (3.0 g) were stirred and heated slowly to 160 °C over 3 h. The reaction was stirred for 30 min at 160 °C and quenched with deionized water (10 mL) and further heated at 95 °C for 24 h. The reaction mixture was neutralized with conc. NaOH and 1 M NaOH to a pH of 5.5. The dark porphyrin mixture was extracted with two portions of ethyl acetate (100 mL), washed with brine solution, and dried over Na_2SO_4. After solvent removal, a purple solid was collected and dried at 60 °C *in vacuo* to yield 0.034 g of porphyrin material (80%). Silica TLC indicated a single spot matching authentic TAPP. ^{1}H NMR (500 MHz; d_6-DMSO; Me_4Si): δ_H, ppm –2.72 (2H, s, pyrrole-NH), 5.59 (8H, s, -NH_2), 8.17 (8H, d, *J* = 8.3, Ph-amino), 7.85 (8H, d, *J* = 8.3, Ph-amino), 8.88 (8H, s, pyrrole-H). MS (MALDI-TOF): *m/z* 674.65. Calcd. for $[C_{44}H_{34}N_8]$ 674.29.

Mixed substituent (4-amino/carboxyphenyl) porphyrins (1a-f). A solution of tetrakis(4-carboxyphenyl)porphyrin **(1a)** (0.52 g, 0.658 mmol) and 39 g of polyphosphoric acid was warmed to 100 °C. To this, 2 equiv. of NH_2OH•HCl (0.108 g, 1.56 mmol) was added and the mixture was slowly heated to 160 °C over 3 h. Upon cooling to room temperature, conc. H_2SO_4 (10 mL) and CH_3OH (80 mL) were added and heated to reflux for 36 h. After the addition, the reaction mixture was neutralized with 1 M NH_4OH to a pH of 5.5. The dark porphyrin solution was extracted with chloroform (~1 L), washed with water, and dried over Na_2SO_4. The solution was evaporated to dryness and dried *in vacuo* overnight affording a dark purple solid (0.48 g, 96% total yield). Silica TLC indicated six porphyrin products (**4a-d**, **2a**, and **1f**) eluting with 4:1 - CH_2Cl_2: ethyl acetate and 2 drops of triethylamine. The amino/ester porphyrins **(4a-d)** were isolated as described below, then hydrolyzed in base using the conditions described above in Route #2 to give **(1b-e)** in good yields.

5-(4-Aminophenyl)-10,15,20-tris(4-carbomethoxyphenyl)porphyrin ($TACM_3PP$ - 4a). Using a preparative silica TLC plate, 0.05 g of the product mixture was applied and eluted with (4:1) CH_2Cl_2: ethyl acetate (2 drops Et_3N) collecting the second band (R_f = 0.68) as $TACM_3PP$, 0.007 g (13% of the original mix). UV-vis (THF): λ_{max}, nm (log ε) 420 (5.13), 516 (3.91), 552 (3.78), 595 (3.54), 648 (3.40). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm –2.79 (2H, s, pyrrole-NH), 3.64 (2H, s, -NH_2), 4.11 (9H, s, -CO_2CH_3), 6.89 (2H, d, *J* = 8.1, Ph-amino), 7.93 (2H, d, *J* = 8.1, Ph-amino), 8.29 (6H, d, *J* = 8.1, Ph-carbomethoxy), 8.44 (6H, d, *J* = 8.1, Ph-carbomethoxy), 8.78 (6H, bs, pyrrole-H), 8.94 (2H, bs, pyrrole-H). MS (ES): *m/z* 804.47 ($[M + H]^+$ calcd. for $[C_{50}H_{38}N_5O_6]$ 804.27).

5,15-Di(4-aminophenyl)-10,20-di(4-carbomethoxyphenyl)porphyrin (*trans*-TA_2CM_2PP, 4b). Using a preparative silica TLC plate, 0.05 g of the product mixture was applied and eluted with (4:1) CH_2Cl_2 : ethyl acetate (2 drops of Et_3N) collecting the third band (R_f = 0.48) as *trans*-TA_2CM_2PP, 0.006 g (12% of the original mix). UV-vis (THF): λ_{max}, nm (log ε) 422 (4.91), 518 (3.72), 557 (3.64), 593 (3.30), 652 (3.26). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm –2.75 (2H, s, pyrrole-NH), 3.65 (4H, s, -NH_2), 4.10 (6H, s, -CO_2CH_3), 7.03 (4H, d, *J* = 7.7, Ph-amino) 7.97 (4H, d, *J* = 7.8, Ph-amino), 8.29 (4H, d, *J* = 7.9, Ph-carbomethoxy), 8.43 (4H, d, *J* = 7.9, Ph-carbomethoxy), 8.77 (4H, d, *J* = 4.0, pyrrole-H), 8.94 (4H, d, *J* = 4.0, pyrrole-H). MS (ES): *m/z* 761.47 ($[M + H]^+$ calcd. for $[C_{48}H_{37}N_6O_4]$ 761.28).

5,10-Di(4-aminophenyl)-15,20-di(4-carbomethoxyphenyl)porphyrin (*cis*-TA_2CM_2PP, 4c). Using a preparative silica TLC plate, 0.05 g of the product mixture was applied and eluted with (4:1) CH_2Cl_2:ethyl acetate (2 drops Et_3N) collecting the fourth band (R_f = 0.40) as *cis*-TA_2CM_2PP, 0.018 (36% of the original mix). UV-vis (THF): λ_{max}, nm (log ε) 420 (5.04), 517 (3.90), 557 (3.81), 594 (3.54), 651 (3.41). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm –2.75 (2H, s, pyrrole-NH), 3.65 (4H, s, -NH_2), 4.11 (6H, s, -CO_2CH_3), 7.07 (4H, d, *J* = 8.3, Ph-amino) 7.99 (4H, d, *J* = 8.3, Ph-amino), 8.29 (4H, d, *J* = 8.2, Ph-carbomethoxy), 8.43 (4H, d, *J* = 8.2, Ph-carbomethoxy), 8.76 (2H, d, *J* = 4.8, pyrrole-H), 8.78 (2H, s, pyrrole-H), 8.94 (2H, s, pyrrole-H), 8.95 (2H, d, *J* = 4.8, pyrrole-H). MS (ES): *m/z* 761.47 ($[M + H]^+$ calcd. for $[C_{48}H_{37}N_6O_4]$ 761.28).

5,10,15-Tris(4-aminophenyl)-20-(4-carbomethoxyphenyl) porphyrin (TA_3CMPP, 4d). Using a preparative silica TLC plate, 0.05 g of the product mixture was applied and eluted with (4:1) CH_2Cl_2:ethyl acetate (2 drops Et_3N) collecting the fifth band (R_f = 0.23) as TA_3CMPP, 0.014 (27% of the original mix). UV-vis (THF): λ_{max}, nm (log ε) 427 (4.83), 520 (3.73), 561 (3.72), 592 (3.45), 655 (3.40). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm –2.76 (2H, s, pyrrole-NH), 3.65 (6H, s, -NH_2), 4.05 (3H, s, -CO_2CH_3), 7.0 (6H, d, *J* = 8.1, Ph-amino) 7.85 (6H, d, *J* = 8.1, Ph-amino), 8.36 (2H, d, *J* = 8.2, Ph-carbomethoxy), 8.40 (2H, d, *J* = 8.2, Ph-carbomethoxy), 8.74 (2H, bs, pyrrole-H), 8.91 (6H,

bs, pyrrole-H). MS (ES): *m/z* 718.53 ([M + H]$^+$ calcd. for [$C_{46}H_{36}N_7O_2$] 718.29.

CONCLUSION

Four meso-subsituted *p*-amino/carboxyphenylporphyrins have been prepared using three different synthetic methods. Two of the methods (Routes #1 and #3) rely on centrifugal or preparative chromatographic separations while a piecewise [2+2] method (Route #2) assembles *trans*-TA_2C_2PP in a straightforward manner requiring no preparative chromatography. A simple carboxy to amino functional group transformation (Route #3) allows for the conversion of TCPP to TAPP or the isolation of a mix of amino/carboxyphenyl substituted porphyrins from a single porphyrin starting material. The target *p*-amino/carboxyphenylporphyrins show a decreased and red-shifted aborbance trend in the visible region with increasing numbers of aminophenyl substituents. Cyclic voltammetry indicates that the energy levels of these materials have sufficiently energetic LUMO levels and well-matched HOMO levels to allow for incorporation in polyaniline dye-sensitized TiO_2 solar cells. The solar conversion efficiency of solid-state polyaniline/TiO_2 solar cells sensitized with *cis*/*trans*-TA_2C_2PP **(1c, 1d)** or TA_3CPP **(1e)** porphyrins is currently under investigation in our laboratory, complementing the reported results with TAC_3PP **(1b)** [10].

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