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# SubPc-ZnPorphyrin conjugates — Synthesis, characterization and properties

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# 1. Introduction

In the recent years, the field of organic solar cells have challenged scientists in various aspects. A great deal of research has been invested towards improving the efficiency of solar cells by not only collecting the solar energy throughout the entire solar spectrum, but also in the effectual conversion of solar energy into resourceful chemical energy [1]. This conversion involves three sequential steps: (i) light absorption, (ii) excitation energy transduction, and (iii) photoinduced electron transfer [2–4]. Notwithstanding, fullerene derivatives are considered to be among the most employed n-type material for photovoltaic applications [5,6]. With exceptional electron accepting properties, they display only weak absorption cross sections in the visible part of the solar spectrum. This alters the sunlight capture, thereby impeding the output of photon-to-electron conversion [7].

In the quest to find promising alternatives to fullerenes, subphthalocyanines (SubPcs) [8,9] have been identified as suitable candidates which possess strong absorption in the visible region with high extinction coefficients. Additionally, subphthalocyanines can play a dual role acting as both electron acceptor and donor

# ABSTRACT

A set of SubPc-Porphyrin dyads and triads have been synthesized by the nucleophilic substitution reaction of hydroxyl-containing *meso*-substituted porphyrins and a good electron acceptor, dodecafluorosubphthalocyanine. Acid-catalyzed condensation of *p*-hydroxybenzaldehyde and the corresponding dipyrromethane, followed by zinc metallation, afforded the appropriate metalloporphyrins. Subsequent nucleophilic substitution occurred between the porphyrin and the axial chlorine atom of the subphthalocyanine when reacted in a sealed tube at 180 °C. The structures of all the synthesized compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy. The photophysical and electrochemical studies have also been performed by using UV–Vis, fluorescence spectroscopy and cyclic voltammetry experiments.

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[10–13], depending on the nature of the counterpart. Due to the synthetic versatility and the tunable properties of the subphthalocyanines, several peripheral substituted derivatives of subphthalocyanines have been prepared [14]. However, there are only a few axially coordinated subphthalocyanine derivatives where the electronic characteristics of the macrocycle are preserved [15–18]. Donor acceptor conjugates of subphthalcyanines are particularly interesting because their excited states can be potentially applied in various molecular electronic devices and artificial photosynthetic systems [12,13]. Furthermore, the incorporated subphthalocyanines impart additional solubility to the conjugates. Thus, in order to achieve highly soluble donor-acceptor conjugates covering a broad range of the solar spectrum, and with increased efficiency of solar energy conversion, the construction of dyads and triads comprised of porphyrin and subphthalocyanine units has been established. A covalently linked B-O bond in the axial position can act as the electron donor and acceptor pair.

Tetraarylporphyrins (A<sub>4</sub>) containing nucleophilic sites in the peripheral positions have been employed as building blocks for various assemblies that are of interest to material scientists and bioinorganic chemists. These assemblies include multiporphyrin arrays [19] and also porphyrins with appended axial ligands. Although many of the *meso*-substituted porphyrins used for such purposes have four identical aryl substituents, less symmetric porphyrins (A<sub>3</sub>B, A<sub>2</sub>B<sub>2</sub>) are expected to permit more varied structures. Particularly, the *trans meso*-A<sub>2</sub>B<sub>2</sub> porphyrins may be utilized to form macrocyclic





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assemblies that are difficult to make from the conventional *meso*-A<sub>4</sub> porphyrins. The construction of trans *meso*-substituted porphyrins containing two –OH groups in the aryl moiety was considered for the convenient nucleophilic substitution with the axial chlorine atom of the subphthalocyanine. Owing to the geometry of the two incorporated SubPc units, the proposed *trans meso*-substituted Porphyrin-SubPc Conjugate was expected to possess improved solubility properties compared to the corresponding monosubstituted derivatives. The present work focusses on the synthesis, characterization and properties of novel A<sub>3</sub>B and trans A<sub>2</sub>B<sub>2</sub> porphyrins, SubPc derivatives, Porphyrin-SubPc dyads and triads.

# 2. Results and discussion

#### 2.1. Synthesis

The synthesis of A<sub>3</sub>B and trans meso-substituted A<sub>2</sub>B<sub>2</sub> porphyrins began with the preparation of dipyrromethane (Scheme 1). Two different dipyrromethanes **1a** and **1b** were synthesized from the corresponding aldehydes (benzaldehyde or methyl 3formylbenzoate) via a condensation with freshly distilled pyrrole in the presence of TFA [20]. Condensation of the dipyrromethanes **1a** or **1b** with *p*-hydroxybenzaldehyde in acetic acid under reflux conditions with air as the oxidant afforded a mixture of A<sub>3</sub>B-(**2a**, 3a) and A<sub>2</sub>B<sub>2</sub>-(2b, 3b), plus a trace of A<sub>4</sub>-(2c, 3c) porphyrins (Scheme 1). Since the base porphyrin intermediates were difficult to handle, conversion to zinc complexes (ZnP) was accomplished with Zn(OAc)<sub>2</sub>,2H<sub>2</sub>O. Initially, with a 1:1 ratio of dipyrromethane **1a** and *p*-hydroxybenzaldehyde, a mixture of monohydroxy triphenyl porphyrin, A<sub>3</sub>B (4a-28%), dihydroxydiphenylporphyrin A<sub>2</sub>B<sub>2</sub> (4b-13%), and tetraphenylporphyrin, A<sub>4</sub> (4c-3%) was isolated [21]. However, in our hands with 1:1.5 ratio of the starting materials, the yield of 4b was increased to 24% and 4a was decreased to 12% while a trace amount of tetraphenylporphyrin A<sub>4</sub> was also isolated.



Scheme 2. Synthesis of -OBu substituted SubPcs.

Adopting similar conditions (ratio 1:1.5), the synthesis of mono (**5a**, 15%), dihydroxy-substituted (**5b**, 26%), and a trace of **5c** derivatives was achieved.

For the synthesis of the OBu-SubPc **6a** (43%), a dinitrile precursor, 4,5-dibutoxyphthalonitrile, was cyclotrimerized with 1 M BCl<sub>3</sub> in *p*-xylene at 160 °C using *o*-dichlorobenzene as the cosolvent (Scheme 2). Attempts were also made to synthesize the SubPc fused dimer by the condensation of dibutoxyphthalonitrile with tetracyanobenzene. To our surprise, we were able to isolate a



Scheme 1. Synthesis of A<sub>3</sub>B and trans meso-substituted A<sub>2</sub>B<sub>2</sub> zinc porphyrins.

butoxy-substituted SubPc derivative, **6b** (22%) containing two active nitrile groups in the peripheral position which can act as a potential building blocks for various supramolecular assemblies. To initiate the formation of a covalent linkage of the SubPc with the ZnP, efforts were taken by reacting SubPc **6a** and ZnP **4b** with/without base (DMAP, DBU, pyridine, NaH, K<sub>2</sub>CO<sub>3</sub>/18-crown-6). However, no product was isolated in any of the conditions. This may be attributed to the electron donating properties of the peripheral butoxy groups in the subphthalocyanine which made the boron atom less electropositive. Studies on the electronic and mechanistic aspects of the different SubPc derivatives led us to investigate the nucleophilic substitution of porphyrin with a good electron acceptor, SubPc-F **(7)**.

Hence SubPc-F (**7**) was synthesized by the cyclotrimerization of tetrafluorophthalonitrile with BCl<sub>3</sub> (1.0 M solution in *p*xylene) using the standard reaction conditions. A conventional nucleophilic substitution required 1:5 M ratio of the Sub-Pc:nucleophile concentration and reflux temperature. The nucleophilic substitution of the chlorine atom by the phenoxy group was first attempted with the monohydroxy substituted ZnP **4a**. Reaction of **7** and **4a** in 1:5 ratio in dry toluene at reflux conditions afforded the product **8** in low yield (12%) after 4 days. However in order to reduce the concentration of nucleophile to a 1:1 M ratio, the reaction was performed in a sealed tube at 180 °C using an equimolar mixture of **4a**:**7** and afforded the SubPc-Porphyrin conjugate **8** in 33% yield (Scheme 3). Adopting



Scheme 3. Synthesis of porphyrin-SubPc-F conjugates.

similar conditions, the reaction of *trans*-  $A_2B_2$  porphyrin **4b** with the SubPc-F **7** gave two products **9a** and **9b** which were isolated by column chromatography. The ester substituted compounds **10a** and **10b** were also prepared employing similar conditions.

In summary, a series of SubPc-Porphyrin conjugates were synthesized by the nucleophilic substitution of the axial chlorine atom by the phenoxy group of the meso-substituted zinc porphyrins. All of the synthesized compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and Mass Spectroscopy.

# 2.2. Optical properties

The electronic interactions between the SubPc and A<sub>3</sub>B/ A<sub>2</sub>B<sub>2</sub>–ZnP were investigated *via* absorption and emission studies. The steady-state absorption spectra of the parent compounds and the conjugates in CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 1(Right A). The absorption spectra of MPP (4a) and DPP (4b) exhibited an intense Soret band at 420 nm and two weak Q bands at 546 nm and 591 nm corresponding to the Zn(II) metalloporphyrin. The SubPc-F moiety also displayed the characteristic Q bands (575 nm, 555 nm-sh) associated with the  $\pi$ - $\pi^*$  transition. The absorption spectra of conjugates [MPS (8), DPPS1 (9a), DPPS2 (9b)] revealed common features of the SubPc-F and ZnP retaining their individual identities in the ground state. The emission spectra of the compounds recorded in CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 1(Right-B). Excitation of the porphyrins DPP and MPP at 420 nm in CH<sub>2</sub>Cl<sub>2</sub> produced two emission bands centered at 597 nm and 644 nm. Whereas excitation of the conjugates displayed diminished intensities of the two bands (MPS, DPPS1 and DPPS2 in Fig. 1).

Additionally, the intensity of the typical Soret band corresponding to the porphyrin moiety is also reduced. The conjugates exhibited altered emission intensities due to charge transfer between the donor metalloporphyrin and the acceptor SubPc-F. In order to confirm this, the fluorescence quantum yields were determined for MPS, DPPS1 and DPPS2 by steady state comparative method using cresyl violet (quantum efficiency,  $\Phi_F = 0.54$ ) [22] as the standard. In comparison to the free SubPc-F, **5** ( $\Phi_F = 0.58$ ), the fluorescence quantum yields of the conjugates decreased significantly (MPS- $\Phi_F$  = 0.089; DPPS2- $\Phi_F$  = 0.082; DPPS1- $\Phi_F$  = 0.063), which correlates well with the fluorescence emission spectra. A similar trend has also been reported in the case of PDI-SubPc Dyad [23]. It is also interesting to note that a more pronounced drop in fluorescence quantum yield was observed in the case of the triad 9a, which contains two SubPc-F units. All these findings suggest the occurrence of a charge transfer process between the ZnP and SubPc species.

#### 2.3. Electrochemical properties

The redox behavior of the dyads and triads was investigated by cyclic voltammetry experiments. The results were compared with those of the reference compounds SubPc-F, MPP and DPP. All experiments were performed at room temperature in deaerated acetonitrile solution containing *tetra-n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>, 0.1 M) as the supporting electrolyte, with glassy carbon as the working electrode, platinum-wire as the counter electrode, and Ag/AgNO<sub>3</sub> as the reference electrode. The representative cyclic voltammograms (CVs) of porphyrins, SubPc-F and SubPc-porphyrin conjugates (MPS, DPPS1 and DPPS2) are shown in Fig. 2. The CVs of the SubPc-Porphyrin conjugates share common features with respect to those of the parent porphyrins, and SubPc-F. SubPc-F presents several characteristic reduction waves of SubPcs with a reversible one electron reduction process occurring at -0.986 V versus Ag/AgNO<sub>3</sub>. In the cathodic direction (between 1 and -2.5 V), MPS showed successive three reduction processes, which are electrochemically reversible, two waves corresponding to the porphyrin (0.481 V and -1.878 V) and one wave corresponding to the SubPc-F located at -0.948 V versus Ag/AgNO<sub>3</sub>.

In comparison to the unsubstituted SubPc-F, the conjugate MPS exhibited a more positive reduction peak ~40 mV vs Ag/AgNO<sub>3</sub> which supports a strong coupling between the subphthalocyanine and the porphyrin units. Moreover, an irreversible oxidation processes was exhibited by the conjugate MPS which occurred at -1.43 V (Table 1). This supports the concept that, in general, the fluoro-subphthalocyanines are difficult to oxidize. The dvad DPPS2 and the triad DPPS1 retain the common features of MPS. A close inspection of the redox features of these compounds reveals that, although the reduction waves based on both porphyrin and SubPc-F do not change significantly, both the oxidative and reductive voltammograms of MPS, DPPS1 and DPPS2 are not exactly the sum of those of the parent SubPc-F and porphyrins. These are good indications that electronic communications between the chromophores are present in the conjugate which can form the Por<sup>+</sup>-SubPc-F<sup>-</sup> species. Thus, the electrochemical investigation confirms the formation of different porphyrin-SubPc conjugates and additionally provide further insights into the electronic properties of the synthesized complexes.

### 3. Experimental

#### 3.1. General

Melting points were determined using a Stuart SMP10 instrument. NMR spectra (<sup>1</sup>H, and <sup>13</sup>C) were acquired in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, or



Fig. 1. Absorption spectra of the compounds in CH<sub>2</sub>Cl<sub>2</sub> at room temperature; (b) emission spectra in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C (420 nm).



**Fig. 2.** Cyclic voltammogram recorded in deareated acetonitrile using TBAPF<sub>6</sub> (0.1 M) as the supporting electrolyte. (a) parent SubPc-F, MPP, DPP: (b) SubPc-poprhyrin Conjugates MPS, DPPS1 and DPPS2.

DMSO using a Varian Inova 400 MHz spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm relative to residual chloroform (<sup>1</sup>H: 7.26 ppm, <sup>13</sup>C: 77.0 ppm), DMSO (<sup>1</sup>H: 2.5 ppm, <sup>13</sup>C: 39.5 ppm), and dichloromethane (<sup>1</sup>H: 5.32 ppm, <sup>13</sup>C: 54.0 ppm). Fourier Transform Infrared measurements were performed on a Varian 800 FT-IR spectrometer. UV-Vis spectra were recorded on Cary 5000 UV-VIS-NIR spectrophotometer. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. The sealed tube reaction was conducted in a unit from Chem Glass, Model 1880. Column chromatography was carried out with silica gel (Sorbent Technologies, 230-400 mesh), and TLC was performed with polyester sheets precoated with silica gel (Sorbent Technologies). Compounds 3-methylformyl benzoate, pyrrole, TFA (Acros *p*-hydroxybenzaldehyde Organics), (Fisher), tetrafluorophthalonitrile (TCI), benzaldehyde, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, 1.0 M BCl<sub>3</sub> solution in *p*-xylene (Sigma Aldrich) were purchased from commercial suppliers and used as received unless otherwise indicated.

# 3.2. General method for the synthesis of porphyrin (A)

A mixture of the dipyrromethane (1.0 equiv) and *p*-hydroxybenzaldehyde (1.5 equiv) was taken in a 250-mL, singlenecked, round-bottomed flask fitted with a condenser and a magnetic stir bar. Acetic acid was added to the reaction mixture, and the resulting pale yellow solution was refluxed with continuous stirring for 7 h. After allowing the thick, black mixture to cool to room temperature, the solvent was removed under vacuum to give a black solid. The solid was then redissolved in dichloromethane and filtered over a pad of silica which was finally washed with THF. The filtrate and washings were combined, and the solvent was evaporated to afford the crude base porphyrin. Without further purification, the crude base porphyrin intermediate was taken to the next step of complexation with zinc.

#### Table 1

Electrochemical properties of SubPc-F, parent porphyrins (MPP, DPP) and SubPc-Porphyrin Conjugates (MPS, DPPS1, DPPS2). The reduction and oxidation potentials presented are in V vs Ag/AgNO<sub>3</sub> at 25 °C.

Compound	$E^1$ (red)	$E^2(red)$	$E^3$ (red)	$E^1(\mathbf{ox})$	$E^2(\mathbf{ox})$	$E^3(\mathbf{ox})$	$E^4(\mathbf{ox})$
SubPc-F	0.265	-0.986	-1.593	-1.541	_	-0.937	0.706
MPP	0.430	-	-1.725	-1.811	-	-0.885	-
DPP	0.421	-0.931	-1.531	-	-	-1.026	0.510
MPS	0.481	-0.948	-1.878	-1.861	-1.431	-0.942	0.538
DPPS1	0.447	-0.919	-1.844	-1.919	-1.424	-0.925	0.493
DPPS2	0.4815	-0.925	-1.96	-1.93	-1.450	-0.953	0.510

# 3.3. General method for the synthesis of porphyrin (B)

Metallation of the base porphyrin was achieved by treating the crude black solid and an excess of  $Zn(OAc)_2 \cdot 2H_2O$  with a 1:1 mixture of  $CH_2Cl_2$ :MeOH (10 volumes w.r.t crude) in a 100-mL, single-necked, round-bottomed flask fitted with a magnetic stirrer at room temperature for 12 h. The progress of the reaction was monitored by TLC. The solvent from the reaction mixture was evaporated, and the residue obtained was extracted with ethyl acetate (10 volumes). The extracts were combined and were washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated to provide a dark purple solid containing a mixture of A<sub>3</sub>B and A<sub>2</sub>B<sub>2</sub> porphyrins. Flash chromatography of the mixture using ethyl acetate:hexane (1:3) afforded pure mono and di-substituted porphyrins.

# 3.4. General method for the synthesis of porphyrin-SubPc-F conjugates (C)

A mixture of porphyrin (1.0 equiv) and dodecafluorosubphthalocyanine (1.0–2.0 equiv) dissolved in dry toluene (10 volumes w.r.t porphyrin) was taken in a sealed tube and heated to 180 °C for 3 days. The progress of the reaction was monitored by TLC. The solvent from the reaction mixture was removed under vacuum and the residue was purified by column chromatography over silica gel using ethyl acetate:hexane in varying ratios.

# 3.5. Synthesis of 5a and 5b

A mixture of dipyrromethane **1b**, (1 g, 0.0035 mol), *p*-hydroxybenzaldehyde (0.653 g, 0.0053 mol), and acetic acid (200 mL) were reacted according to general procedure A. This was then followed by the metallation with  $Zn(OAc)_2 \cdot 2H_2O(1.53 \text{ g}, 0.007 \text{ mol})$  in CH<sub>2</sub>Cl<sub>2</sub>:MeOH solution (50 mL, 1:1) according to the standard procedure B to afford a mixture of A<sub>3</sub>B and *trans* A<sub>2</sub>B<sub>2</sub> porphyrins corresponding to the mono hydroxyl **5a** and di-hydroxy porphyrins 5b, respectively. Purification of the mixture by column chromatography using ethyl acetate:hexane (1:3) afforded pure **5a** and **5b**. **5a**: yield: 0.46 g (15%), **mp**: >250 °C. **IR** (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3052, 2989, 1719, 1484, 1422, 1264, 1170, 1109, 735, 709. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.95 (*d*, *J* = 4.8, 2H), 8.86 (*m*, 9H), 8.42 (*d*, *J* = 8 Hz, 3H), 8.39 (*d*, *J* = 8 Hz, 3H), 8.02 (*d*, *J* = 7.2 Hz, 2H), 7.80 (*t*, *J* = 7.6 Hz, 3H), 7.12 (d, J = 7.2 Hz, 2H), 3.92 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.2, 157.3, 150.6, 149.3, 143.5, 138.9, 135.3, 134.7, 133.4, 132.4, 131.3, 128.4, 128.3, 127.9, 121.9, 121.3, 119.1, 114.0, 52.8. MS (MALDI-TOF) *m*/*z* for C<sub>50</sub>H<sub>34</sub>N<sub>4</sub>O<sub>7</sub>Zn: Calcd: 868.2132; Found: 868.2654. **5b**: yield: 0.76 g (26%). **mp**: >250 °C. **IR** (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3055, 2985, 1721, 1422, 1264, 1169, 895.53, 734, 707, 619. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  9.97 (s, broad, 1H), 8.84 (d, I = 4.8, 4H), 8.69 (d, *J* = 4.8 Hz, 4H), 8.67 (*s*, 2H), 8.43 (*d*, *J* = 8 Hz, 2H), 8.38 (*d*, *J* = 8 Hz, 2H), 7.93–7.96 (*m*, 6H), 7.15 (*d*, *J* = 8.8 Hz, 4H), 3.92 (*s*, 6H). <sup>13</sup>**C NMR** (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  167.1, 157.4, 150.5, 149.4, 143.7, 138.8, 135.9, 134.5, 133.6, 132.6, 131.6, 128.8, 128.5, 127.8, 121.8, 121.4, 119.2, 114.1, 52.9. **MS** (MALDI-TOF) *m/z* for C<sub>48</sub>H<sub>32</sub>N<sub>4</sub>O<sub>6</sub>Zn: Calcd: 826.1716; Found: 826.1532.

# 3.6. Synthesis of Ga

A solution of dicyanodibutoxybenzene (0.819 g, 3.0 mmol) in odichlorobenzene (20 mL) under Ar blanket was placed in a 100-mL, two-necked, round-bottomed flask fitted with a condenser, a gas inlet, and a stir bar. Boron trichloride (1 mL, 1 M solution in pxylene) was then added dropwise, maintaining the temperature between 25–30 °C. The reaction mixture was heated to reflux at 160 °C for 5 h. The solution slowly turned from a pale yellow to a deep red colored solution upon refluxing. After cooling to room temperature, the mixture was passed through a plug of silica gel, followed by washing the plug with CH<sub>2</sub>Cl<sub>2</sub> to remove impurities and then with THF to extract the product. The organic extract was dried, (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to dryness. Column purification of the crude product using ethyl acetate:hexane (1:1) afforded 10 as a pink solid; yield: 1.11 g (43%). **mp**: > 300 °C. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.20 (s, 4H), 4.29–4.40 (m, 10H), 1.96–2.01 (q, J = 7.4 Hz, 8H), 1.51–1.62 (q, J = 7.6 Hz, 8H), 1.06–1.08 (q, J = 7.6 Hz, 20H). <sup>13</sup>C **NMR** (100 MHz, CDCl<sub>3</sub>): δ 148.2, 146.0, 145.6, 145.4, 144.1, 141.4, 119.3, 114.8. **MS** (MALDI-TOF) *m*/*z* for C<sub>48</sub>H<sub>60</sub>BClN<sub>6</sub>O<sub>4</sub>: Calcd: 862.4356; Found: 862.4903.

# 3.7. Synthesis of 6b

Dry dicyanodibutoxybenzene (1.22 g, 4 mmol) and tetracyanobenzene (0.1 g, 0.05 mmol) were placed in a 100-mL, two-necked, round-bottomed flask fitted with a condenser, gas inlet, and a stir bar. The system was flushed with argon for ~10 min to remove air and moisture. Boron trichloride (2 mL, 1 M solution in *p*-xylene) was then added dropwise, maintaining the temperature between 25-30 °C. The mixture was stirred at 140 °C for 7 h. A change of color was observed from pale yellow, to pink and to a final thick, reddish-blue solution. After cooling, the solvent was evaporated to give a dark blue solid which was chromatographed by eluting with ethyl acetate:hexane (1:10) to afford **6b** as reddish blue solid; yield: 0.66 g (22%).**mp**: >250 °C. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.25 (s, 2H), 8.20 (s, 4H), 4.29-4.40 (m, 10H), 1.96-2.01 (m, 8H), 1.51-1.62 (m, 8H), 1.06–1.08 (*m*, 20H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 155.2, 153.4, 152.7, 151.1, 143.8, 129.1, 128.7, 126.5, 124.6, 116.1, 112.3, 105.0, 104.6, 69.4, 31.0, 31.0, 19.2, 13.9. MS (MALDI-TOF) m/z for C<sub>48</sub>H<sub>60</sub>BClN<sub>6</sub>O<sub>4</sub>: Calcd: 768.3111; Found: 768.4312.

# 3.8. Synthesis of 8

A mixture of **4a** (0.026 g, 0.03 mol) and **7** (0.025 g, 0.03 mmol) was reacted in dry toluene (2 mL) using a sealed tube according to the general procedure C. Repeated washing of the product with pentane and drying under vacuum did remove all of the solvent impurities and water; yield: 16.3 mg (33%). **mp**: >250 °C. **IR** (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3058, 2924, 2853, 1531, 1480, 1264, 1107, 1002, 965, 798, 741. <sup>1</sup>**H NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.94 (*s*, 4H), 8.92 (*d*, *J* = 4.8, 2H), 8.70 (*d*, *J* = 4.4 Hz, 2H), 8.20 (*d*, *J* = 6.8 Hz, 6H), 7.75–7.78 (*m*, 9H), 7.64 (*d*, *J* = 8 Hz, 2H), 5.73 (*d*, *J* = 8 Hz, 2H). <sup>13</sup>**C NMR** (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  151.5, 150.5, 148.8, 144.2, 143.0, 142.2, 137.4, 135.4, 132.2, 131.9, 127.8, 126.9, 121.4, 120.4, 117.4, 115.5. **MS** (MALDI-TOF) *m/z* for C<sub>68</sub>H<sub>27</sub>BF<sub>12</sub>N<sub>10</sub>OZn: Calcd: 1304.1719; Found: 1304.1516.

### 3.9. Synthesis of **9a** and **9b**

A mixture of 4b (0.055 g, 0.07 mmol) and 7 (0.1 g, 0.154 mmol) was reacted in dry toluene (2 mL) using a sealed tube according to the general procedure C. Repeated washing of the products with pentane and drying under vacuum did remove all of the solvent impurities and water. **9a**: vield: 14 mg (10%). **mp**: >250 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3052, 2925, 2854, 1531, 1480, 1265, 1095, 1003, 964, 799, 740. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.90 (*d*, *J* = 4.4 Hz, 4H), 8.67 (*d*, *J* = 4.8, 2H), 8.18 (*d*, *J* = 6.4 Hz, 4H), 7.76–7.81 (*m*, 6H), 7.63 (*d*, *J* = 6.8 Hz, 4H), 5.73 (*t*, *J* = 8.8 Hz, 4H). <sup>13</sup>**C NMR** (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 151.5, 150.4, 148.8, 144.5, 144.2, 142.9, 141.1, 141.4, 137.4, 135.4, 134.7, 1322.2, 131.9, 132.2, 131.9, 127.9, 126.9, 121.4, 120.4, 117.4, 115.5. **MS** (MALDI-TOF) *m/z* for C<sub>92</sub>H<sub>26</sub>B<sub>2</sub>F<sub>24</sub>N<sub>16</sub>O<sub>2</sub>Zn: Calcd: 1930.1675; Found: 1930.1643. **9b:** yield: 23 mg (23%). **mp**: >250 °C. **IR** (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3053, 2924, 2854, 1531, 1481, 1264, 1224, 1094, 1000, 965, 799, 740. <sup>1</sup>H **NMR** (400 MHz,  $CD_2Cl_2$ ):  $\delta$  8.97 (*d*, *J* = 4.8 Hz, 2H), 8.92 (*d*, *J* = 4.8, 2H), 8.90 (d, J = 4.8 Hz, 2H), 8.69 (d, J = 4.8 Hz, 2H), 8.18 (d, *J* = 7.2 Hz, 4H), 8.04 (*d*, *J* = 8.4 Hz, 2H), 7.75–7.80 (*m*, 6H), 7.64 (*d*, J = 8.4 Hz, 2H), 7.20 (t, J = 6.4 Hz, 2H), 5.77 (d, J = 8.4 Hz, 2H). <sup>13</sup>C **NMR** (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 155.6, 151.2, 150.7, 150.3, 150.2, 148.6, 144.3, 143.9, 142.9, 141.6, 141.1, 137.3, 135.7, 135.2, 134.6, 132.1, 131.7, 127.6, 126.7, 121.2, 120.1, 117.3, 115.3, 113.6. MS (MALDI-TOF) *m*/*z* for C<sub>68</sub>H<sub>27</sub>BF<sub>12</sub>N<sub>10</sub>O<sub>2</sub>Zn: Calcd: 1320.1668; Found: 1320.1418.

# 3.10. Synthesis of 10b

A mixture of **5b** (0.064 g, 0.077 mmol) and **7** (0.1 g, 0.154 mmol) was reacted in dry toluene (2 mL) in a sealed tube according to the general procedure C. Repeated washing of the product with pentane and drying under vacuum did remove all of the solvent impurities and water; yield: 24 mg (22%). **mp**: >250 °C. **IR** (CH<sub>2</sub>Cl<sub>2</sub>) cm<sup>-1</sup>: 3058, 2924, 2854, 1532, 1483, 1392, 1265, 1223, 1169, 1114, 995, 966, 797, 741, 718. <sup>1</sup>H **NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.95 (*d*, *J* = 4.4 Hz, 2H), 8.84 (*d*, *J* = 4.8 Hz, 2H), 8.83 (*d*, *J* = 4.8 Hz, 2H), 8.80 (*s*, 2H), 8.69 (*d*, *J* = 4.8 Hz, 2H), 8.42 (*d*, *J* = 8.4 Hz, 2H), 8.40 (*d*, *J* = 7.8 Hz, 2H), 8.01 (*d*, *J* = 7.8 Hz, 2H), 7.15 (*d*, *J* = 8.4 Hz, 2H), 5.72 (*d*, *J* = 7.8 Hz, 2H), 3.91 (*s*, 6H). <sup>13</sup>**C NMR** (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  167.5, 155.9, 151.0, 150.3, 144.1, 143.1, 138.1, 135.1, 132.6, 132.1, 131.9, 129.1, 127.1, 120.1, 117.4, 115.4, 113.5, 52.5. **MS** (MALDI-TOF) *m*/*z* for C<sub>72</sub>H<sub>31</sub>BF<sub>12</sub>N<sub>10</sub>O<sub>6</sub>Zn: Calcd: 1436.1777; Found: 1436.1654.

### 4. Conclusions

We have synthesized different SubPc-Zn-Porphyrin conjugates which are linked in the axial position. All the synthesized compounds were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy and their properties have been studied by absorption, emission spectroscopy and electrochemical measurements. The electrochemical measurements, coupled with the emission results, demonstrate the existence of the electronic communication occurring between the SubPc and the porphyrin moieties. The synthesized ZnP-SubPc conjugates are expected to find applications in artificial photosynthetic systems and various molecular electronic devices.

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