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# Synthesis and characterization of three covalently linked porphyrin-phthalocyanine pentamers with nucleophilic substitution

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ABSTRACT

In this paper the synthetic methods of three covalently linked porphyrin-phthalocyanine heteropentamers, containing four units of porphyrin linked to a central phthalocyanine (Mpor-LPc; M = 2H, Fe, L = Zn, Fe), are described. The synthetic strategy is on the basis of nucleophilic substitution reactions between [1,8,15,22-tetra nitro phthalocyanines] and [5-(4-hydroxy phenyl)-10,15,20-triphenyl porphyrins] as the phenolic alcohols. Porphyrins are linked with oxygen as spacer through meso position of phenyl group to phthalocyanines. These macromolecules were characterized by $^{1}$H NMR, UV–Vis, IR, fluorescence and mass spectroscopy. The electronic absorption spectrums of the hetero-dyad systems changed significantly upon coupling and showed a great red shift in the phthalocyanine Q-bands. These changes confirm the electron-donating effects of the porphyrin units and the extension of conjugated π-systems. The emission spectra of the products supports intramolecular energy and charge transfer between the sub-units.

## 1. Introduction

Porphyrins and phthalocyanines represent two related groups of very versatile macrocyclic organic molecules. Metalloporphyrins are widely studied as biomimetic models for several biological redox processes [1], and have been extensively used in chemical, electrochemical [2] and photochemical analyses.

Metallophthalocyanines are widely used molecules in electrocatalyst [3], infrared sensors [4], and nonlinear optics [5] and photodynamic therapy agents [6,7]. They can also be useful for oxygen reduction in fuel cell technology [8].

Conjugates of porphyrins and phthalocyanines are very interesting structures for various reasons. The most important reason is that these macrocycles have complementary absorptions in the visible region and the emission spectra of phthalocyanines do not show significant overlap with those of the porphyrins. The fluorescence quantum yields of phthalocyanines are 6–10 times higher than porphyrins [9]. Another reason is the stability of these molecules. Phthalocyanines are generally more stable and more rigid than porphyrins, so they oxidize harder. As a result the electrochemical oxidation of a porphyrin can be performed in the presence of phthalocyanines. So these conjugates are good choices for usage in molecular photonics, catalysis and light harvesting architectures with a good spectral coverage in the blue and red wavelengths [9].

Different synthetic strategies have been used to prepare multi porphyrin-phthalocyanine arrays. These methods are based on electrostatic interactions in molecules with opposite charges, host–guest interactions [10], the axial coordination [11] and covalent linking's by using functional groups [12–16].

The covalent linking of phthalocyanines to porphyrins was first achieved by Gaspard and co-workers [17]. A dimmer of these compounds with one porphyrin unit linked to a phthalocyanine unit was shown to exhibit interesting charge transfer properties [18]. Phthalocyanine-porphyrin nonamers as a mixture of isomers of tetra substitution of porphyrin dimmers have also been prepared [19]. These arrays are stable enough against oxidant or reductant agents [20,21] and can be used as multi-nuclear catalysts.

In this paper we report the synthesis, characterization and spectral properties of covalently linked pentamers, one phthalocyanine and four porphyrins linked through an oxy-bridge. Oxygen atoms fully conjugate the five major π systems and improve the efficiency of the electron and energy transfer processes.

The synthesis started from the corresponding functionalized metalloporphyrins (with one OH group) and metallophthalocyanines (with four $NO_2$ group) instead of the synthetic route involving the self-cyclization reaction of phthalonitrile derivatives which Nyokong and co-workers had been used [21]. For synthesis of nitrophthalocyanines (**2a** and **2b**) we used 3-nitrophthalonitrile instead of 4-nitrophthalonitrile used in Nyokong's works. This compound broaden UV–Vis spectrum coverage of pentamers and larger Q-bands shifts about 50–78 nm observed that have not been reported before. Our method gives high yields relative to starting

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used porphyrins and phthalocyanines. This synthetic strategy can be applied to prepare mixed metal arrays with high yields and will be useful for the preparation of other substituted phthalocyanines and has not been reported previously.

## 2. Experimental

### 2.1. General

UV–Vis spectra were recorded on a Shimadzu UV–Vis 2100 spectrophotometer. The IR spectrums were recorded on a Bomem-MB102 FT-IR spectrometer. $^1$H NMR and $^{13}$C NMR spectra were recorded using a Bruker 300 MHz NMR. MALDI-TOF measurements were performed with a Kratos Kompakt mass spectrometer. A nitrogen laser (337 nm) was used for desorption and ionization with an accelerating voltage of 20 kV. Ions were detected as positive on a time-of-flight mass detector in the reflector mode. Dithranol was used as a matrix and LiBr was used as cationating agent. Elemental analyses were performed on a LECO CHNS 932 instrument. Fluorescence emission spectra were performed with a Varian Cary Eclipse spectrofluorometer.

### 2.2. Chemicals

Pyrrole, benzaldehyde, 4-hydroxy benzaldehyde, potassium carbonate, iron (II) chloride, zinc acetate, silica gel 60 for chromatography and DMF were purchased from Merck.

1,8,15,22-Tetra nitro zinc (II) phthalocyanine (**2a**) and 1,8,15,22-tetra nitro iron (II) phthalocyanine (**2b**), were synthesized as reported in the literature [22]. All solvent were dried using standard methods prior to use.

### 2.3. Synthesis

#### 2.3.1. [5-(4-Hydroxy phenyl)-10,15,20-triphenyl porphyrin] (*1a*) and [5-(4-hydroxy phenyl)-10,15,20-triphenyl porphyrin] iron (III) chloride (*1b*)

A mixture of 4-hydroxybenzaldehyde (10 mmol, 1.25 g) and benzaldehyde (30 mmol, 3 cm$^3$) were added to 80 cm$^3$ propionic acid, under nitrogen atmosphere. Pyrrole (40 mmol, 2.8 cm$^3$) was added and the resulting mixture was refluxed for 1 h. After cooling to room temperature, the mixture was filtered and washed three times with hot water. Column chromatography on silica gel was performed with dichloromethane/*n*-hexane (1:1) as eluent The first major cut was TPP and the second cut was found to be (**1a**) [26]. Evaporation of the solvent resulted 0.6 g (10%) of a purple solid **1a**. UV–Vis (DMF): $\lambda_{max}$/nm (log $\varepsilon$): 420(5.4), 517(4.4), 550(4.1), 590(4.0), 654(4.2). $^1$H NMR (300 MHz, DMSO-d$_{6,}$ 25 °C) : $\delta$, ppm −2.91 (s, 2H, N–H), 7.21–7.23 (d, 2H, phenyl H), 7.74–7.75 (m, 9H, phenyl H), 8.01–8.05 (d, 2H, phenyl H), 8.25–8.28 (d, 6H, phenyl H), 8.75–8.78 (d, 6H, pyrrole H), 8.90–8.92 (d, 2H, pyrrole H), 9.96 (s, 1H, OH). MALDI-TOF-MS: *m/z:* 636.36 [M+Li−H]$^+$. *Anal.* Calc. for $C_{44}H_{30}N_4O$: C, 83.82; H, 4.75; N, 8.88. Found: C, 83.75; H, 4.79; N, 8.91%.

A mixture of **1a** (2 mmol, 1.26 g) and iron (II) chloride (4 mmol, 0.795 g) in 30 cm$^3$ dimethylformamide DMF was heated at 100 °C for 2 h while stirring under nitrogen for preventing μ-oxo dimer formation [23]. Removal of DMF by evaporation resulted in a purple solid that was washed with an adequate amount of water in order to eliminate the of extra iron chloride (II). The MALDI-TOF mass spectra showed only a monomeric molecular ion peak, indicating absence of μ-oxo dimer. The crude product (**1b**) was recrystallized from dichloromethane with methanol and produced 87% yield. UV–Vis (DMF): $\lambda_{max}$/nm (log $\varepsilon$): 419(5.2), 512(4.5), 588(4.3). $^1$H NMR (300 MHz, DMSO-d$_6$) paramagnetic, $\delta$ 72.8 (H pyrrole), 80.1 (H pyrrole) with the ratio of 3:1.$^1$H NMR (300 MHz, CDCl$_3$) paramagnetic, 81.2 (H pyrrole), 12.2 (meta H phenyl), 13.4 (meta H phenyl), 6.3 (para H phenyl), 8.0 (ortho H phenyl). MALDI-TOF-MS: *m/z:* 690.15 [M+Li−H−Cl]$^+$. *Anal.* Calc. for $C_{44}H_{28}N_4OFeCl$: C, 73.42; H, 3.89; N, 7.78. Found: C, 73.21; H, 3.92; N, 7.71%.

#### 2.3.2. Tetrakis [5-phenoxy-10,15,20, triphenyl porphyrin] zinc (II) phthalocyanine (*3a*)

A mixture of **2a** (0.025 mmol, 0.02 g), **1a** (0.2 mmol, 0.126 g) and dry $K_2CO_3$ (0.2 mmol, 0.027 g) in 20 cm$^3$ dry DMF was refluxed under nitrogen atmosphere for 6 h, and then $K_2CO_3$ was separated by filtration. After the solvent evaporated, column chromatography on basic alumina was performed. $CH_2Cl_2$ was used as an eluent and nonreacted porphyrins were separated as the first cut. Toluene: DMF mixture was used as a more polar solvent. By using solvent mixtures that contained increasingly 10–25% DMF two separated band were isolated. The first was a mixture of statistic products and the second cut was the desired product with 52% yield. UV–Vis (DMF): $\lambda_{max}$/nm (log $\varepsilon$): 421(5.4), 517(4.4), 550(4.1), 589(4.0), 654(4.2), 722(4.4). $^1$H NMR (300 MHz, DMSO-d$_6$) the spectrum was similar to **1a** in addition to $\delta$: 7.6–7.6 (phthalocyanine H). IR (KBr): $v_{max}$, cm$^{-1}$: 1261(aromatic C–O–C). MALDI-TOF-MS: *m/z:* 3097.05 [M+Li−H]$^+$. *Anal.* Calc. for $C_{208}H_{128}N_{24}O_4Zn$: C, 80.80; H, 4.14; N, 10.86. Found: C, 80.74; H, 4.18; N, 10.91%.

#### 2.3.3. Tetrakis [5-phenoxy-10,15,20, triphenyl porphyrin iron (III) chloride] zinc (II) phthalocyanine (*3b*)

A mixture of **2a** (0.025 mmol, 0.02 g), **1b** (0.2 mmol, 0.136 g) and dry $K_2CO_3$ (0.2 mmol, 0.027 g) in 20 cm$^3$ DMF was refluxed under nitrogen atmosphere for 6 h and then $K_2CO_3$ was separated by filtration. After the solvent evaporated, column chromatography on basic alumina was performed according to the method used for **3a** and **3b** with 55% yield. UV–Vis (DMF): $\lambda_{max}$/nm (log $\varepsilon$): 419(5.4), 572(4.3), 512(4.2), 750(4.5), $^1$H NMR (300 MHz, DMSO-d$_6$) paramagnetic, $\delta$ 79.24 (6H, pyrrole H), 72.10 (2H, pyrrole H). $^1$H NMR (300 MHz, CDCl3), $\delta$ 81.4 (8H, pyrrole H), 13.5 (3H, meta phenyl H), 12.8 (1H meta phenyl H), 12.3 (3H, meta phenyl H), 11.7 (1H meta phenyl H). IR (KBr): $v_{max}$, cm$^{-1}$: 1261 (aromatic C–O–C). MALDI-TOF-MS: *m/z:* 3324.12 [M+3Li−3H−4Cl]$^+$ *Anal.* Calc. for $C_{208}H_{120}N_{24}O_4Cl_4Fe_4Zn$: C, 72.43; H, 3.47; N, 9.74. Found: C, 72.51; H, 3.49; N, 9.79%.

#### 2.3.4. Tetrakis [5-phenoxy-10,15,20, triphenyl porphyrin iron (III) chloride] iron (II) phthalocyanine (*3c*)

A mixture of **2b** (0.025 mmol, 0.02 g), **1b** (0.2 mmol, 0.136 g) and dry $K_2CO_3$ (0.2 mmol, 0.027 g) in 20 cm$^3$ DMF was refluxed under nitrogen atmosphere for 6 h. The solvent evaporated and column chromatography was performed according to the method used for **3a** and **3c** collected in 50% yield. UV–Vis (DMF): $\lambda_{max}$/nm (log $\varepsilon$): 419(5.5), 573(4.6), 619(4.4), 652(4.5) 725(4.6). $^1$H NMR (300 MHz, DMSO-d$_6$) paramagnetic, $\delta$ 83.5 (8H, pyrrole H). IR (KBr): $v_{max}$, cm$^{-1}$: 1261(aromatic C–O–C). MALDI-TOF-MS: *m/z:* 3302.88 [M+Li−H−4Cl]$^+$. *Anal.* Calc. for $C_{208}H_{120}N_{24}O_4Cl_4Fe_5$: C, 72.63; H, 3.48; N, 9.77. Found: C, 72.65; H, 3.49; N, 9.76%.

## 3. Results and discussion

In this article we used nucleophilic aromatic substitution reactions for the synthesis of substituted phthalocyanines in terms of the leaving groups and nucleophiles used. $NO_2$ is a good leaving group for nucleophilic aromatic substitution reactions. In the $S_NAr$ mechanism the rate determining step involves formation of a tetrahedral intermediate and its formation is promoted by the leaving groups having strong electron withdrawing effects such as $NO_2$ [24].