

## Synthesis of porphyrins as precursors to PAMAM dendrimers and their metal chelating properties

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### ABSTRACT

Novel meso-porphyrins were synthesized via microwave assistance and implemented as centers to polyamide amine (PAMAM) dendrimers. The molecular structures of the porphyrins were characterized by UV-Vis, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. In addition, porphyrin-PAMAM dendrimers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The molecular weight of the prepared dendrimers were confirmed by MALDI-TOF mass spectrometry. These porphyrin-core-PAMAM-modified dendrimers were used as templates to form Ag<sup>0</sup> species and doped nylon membranes, using the XPS technique to confirm the chemical reduction of the metal cation.

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### 1. Introduction

Often, the simplest heterocyclic compounds have been used as primary-block-building units for most complex macromolecules [1]. As it is well known, pyrrole (azole) is a fundamental piece of the basic structure of porphyrins. As a matter of fact, porphyrins are compounds where four pyrrole subunits are linked via the  $\alpha$ -positions through four methine groups. Porphyrins are widely distributed in nature, frequently, as complexes with metallic cations like Fe(II), Mg(II), Cu(II), etc. [2-3]. The chemistry of porphyrins occupies an important place in the history of organic chemistry. The most important method for the synthesis of porphyrins is undoubtedly the Rothmund synthesis; others are the Adler and Lindsey methods. In summary, porphyrin syntheses have been carried out using corrosive, high boiling point solvents or

large volumes of a halogenated solvent containing Lewis acids [4-5].

The microwave assisted synthesis of porphyrins is a viable option because it can be carried out under no-solvent-reaction conditions with yields that are better than those obtained by convectional heating. It has been reported that during the synthesis of tetraphenyl porphyrins by microwave heating, using silica gel as a solid support, pyrrole and benzaldehyde react [6-7]. When microwaves are used as an energy source, the temperature is increased rapidly because the entire sample is heated, and the reaction between the starting materials is promoted, where a short reaction time is one of the obtained benefits [8-9].

The introduction of porphyrins into dendritic structures began mainly as core entities due to the morphological resemblance of these macrostructures to natural hemo-proteins [10]. Over the years, porphyrin macrocycles have also

been introduced as surface groups either within the dendritic branches or spread throughout the entire molecule architecture [11-12]. Porphyrin dendrimers are hybrid molecules to be used in biomimetics, artificial photosynthesis, catalysis with biomedical applications and optoelectronics [13]. Recent studies include the appendage of metal redox centers, which are important for some regiospecific catalytic properties; on the other hand, the incorporation of porphyrins into dendrimers has shown an unusual photophysical and electrochemical redox behavior [14-15].

The porphyrin-core dendrimers have been studied because the terminal substituent groups on the photoactive core can modulate their physicochemical properties. This fact has been extensively studied for a number of different applications such as catalysts, organic solar cells, photoelectron-chemical devices, light-emitting diodes, and photodynamic therapy [16]. Different classes of dendrimers bearing 8 and 32 fluorene donor groups have been synthesized, and UV-vis spectra have confirmed that the individual properties of donor and acceptor moieties are preserved; on the other hand, the efficient energy transfer shown by these dendrimers has been evidenced by fluorescence spectroscopy studies [17].

PAMAM dendrimers have been functionalized using a resorcinarene core, and it has been found that by this functionalization, it is possible to obtain nickel and copper retentions of 35 and 70 %, respectively, in neutral-pH aqueous solutions at room temperature. In addition, a study of trialkylamine compounds has shown that the retention of metal cations such as nickel, copper, lead, zinc, and cobalt from an aqueous solution with an initial concentration of 25 ppm at room temperature and neutral pH can be highly efficient: for Ni (II), the efficiency was up to 96.00 %; for Pb (II), it ranged from 93.00 to 99.00 %; and for Cu (II), it almost reached 100 % [18-19]. The use of dendrimers as templates for the synthesis of metal particles is a promising methodology with applications in either the catalysis field or as chemical sensors due to the globular and controlled structure of these molecules [20-22]. PAMAM dendrimers are the most widely used compounds for these purposes because their structure and composition are uniform, so the obtained metallic particles are encapsulated inside the dendrimer and kept stable due to a steric impediment without being passivated [23].

The method for obtaining metal particles encapsulated in dendrimers consists of two steps: the addition of metal cations to the dendrimer structure and the chemical reduction of these cations to obtain neutral metal atoms. The synthesis of Au, Pd, Pt and Ag particles has been reported for this method [24-25]. In this sense, metallic silver particles are of great interest due to their good conductivity, chemical stability and catalytic and antibacterial activity in addition to other biomedical applications such as antivirals and fungicides [26-27]; furthermore, silver particles are important catalysts in the production of major industrial chemicals because these metal atoms are not affected by the reaction, and they are almost completely recovered after being used [28].

## 2. Experimental

### 2.1. Instrumentation

Solvents and reagents were purchased from Aldrich and used without further purification. Infrared spectra were recorded on a Nicolet FT-IR Magna 700 spectrometer.  $^1\text{H}$  (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) spectra were recorded on a JEOL Eclipse-300 equipment in  $\text{CDCl}_3$ , and chemical shifts are expressed in ppm relative to tetramethylsilane used as internal standard. Mass spectra were recorded on a Micromass ToFSpec (MALDI-TOF) using 2,5-dihydroxybenzoic acid (DHB) as matrix. The X-ray photoelectron spectroscopy allowed to perform a surface-sensitive-quantitative-spectroscopic and

elemental analysis. The same reactions were performed by a microwave device Monowave 300 Anton PARR.

### 2.2. Synthesis

#### 2.2.1. Tetraphenyl porphyrin with four active points (3a and 4a)

**Compound 3a:** 2-Methoxy benzaldehyde (0.6856 g, 5 mmol) was added to pyrrole (0.3354 g, 5 mmol) at 70 °C, using a microwave reactor Monowave 300 with constant stirring for 2 h. The presence of porphyrin (**3a**) was corroborated by means of thin layer chromatography and it was continued by column chromatography purification. An intense purple powder was obtained (Scheme 1). Color: Deep purple. Yield: 10%. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3330, 1603, 1501, 1240, 1170, 998, 750. UV/Vis ( $\text{CH}_3\text{OH}$ ,  $\lambda_{\text{max}}$ , nm): 230, 420, 525, 550, 600, 650.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): -2.82 (s, 2H, pyrrole int.), 3.83 (s, 12H,  $\text{OCH}_3$ ), 6.94-7.27 (m, 8H, Ar-H), 8.01 (br, 8H, Ar-H), 8.34 (br, 8H, pyrrole).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 56.2 (O- $\text{CH}_3$ ), 99.13 (methine), 111.4 (Ar), 119.9 (Ar), 120.7 (pyrrole), 120.9 (Ar), 128.9 (Ar), 142.1 (pyrrole), 156.65 (Ar-porphyrin), 161.1 (pyrrole). MALDI-TOF ( $m/z$ ): 734. Anal. calcd. for  $\text{C}_{48}\text{H}_{38}\text{N}_4\text{O}_4$ : C, 78.45; H, 5.21; N, 7.62. Found: C, 77.29; H, 5.67; N, 7.47%.

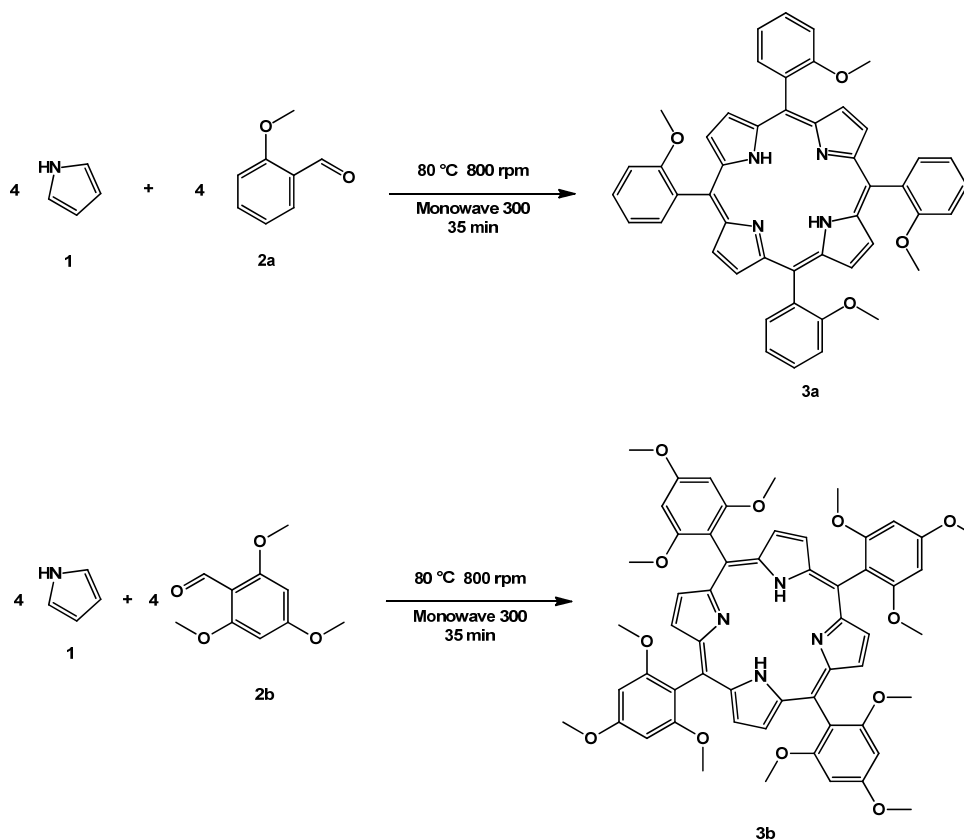
**Compound 4a:** Afterwards, porphyrin **3a** (0.1 g, 0.136 mmol) was added to 50 mL of dichloromethane at 100 °C, obtaining a homogeneous solution. Later, it was cooled at 0 °C to add  $\text{BBr}_3$  (0.1363 g, 0.5443 mmol). The reaction was kept under constant stirring for 24 h. The product was dried in a rotary evaporator and later, it was precipitated using a dichloromethane-hexane solution (1:1, v:v), obtaining the unprotected porphyrin **4a** (Scheme 1). Color: Deep purple. Yield: 97%. UV/Vis ( $\text{CH}_3\text{OH}$ ,  $\lambda_{\text{max}}$ , nm): 200, 230, 420, 525, 550, 600, 650. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3580, 1603, 1501, 1240, 1070, 998, 750.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -2.82 (s, 2H, pyrrole int.), 5.35 (s, 4H, O- $\text{CH}_3$ ), 6.94-7.27 (m, 8H, Ar), 8.01 (br, 8H, Ar), 8.34 (a, 8H, pyrrole).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 99.13 (methine), 111.4 (Ar), 119.9 (Ar), 120.7 (pyrrole), 120.9 (Ar), 128.9 (Ar), 142.1 (pyrrole), 156.65 (Ar-porphyrin), 161.1 (pyrrole). MALDI-TOF ( $m/z$ ): 678.23. Anal. calcd. for  $\text{C}_{44}\text{H}_{30}\text{N}_4\text{O}_4$ : C, 77.86; H, 4.46; N, 8.25. Found: C, 77.63; H, 5.11; N, 8.29%.

#### 2.2.2. Tetraphenyl porphyrin with twelve active points (3b and 4b)

2,4,6-Trimethoxy benzaldehyde (0.1 g, 5 mmol) and trifluoroacetic acid (0.149 g, 1.3067 mmol) were added to 50 mL of dichloromethane at 70 °C and constant stirring. Afterwards, pyrrole (0.3354 g, 5 mmol) was added and the reaction continued at room temperature for 72 h. Finally, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.135 g, 5 mmol) was added at room temperature and the reaction was carried out for 24 h more. The presence of porphyrin was corroborated by thin layer chromatography and it was purified by column chromatography (Scheme 1).

**Compound 3b:** Color: Reddish powder. Yield: 13 %. UV/Vis ( $\text{CH}_3\text{OH}$ ,  $\lambda_{\text{max}}$ , nm): 220, 301, 418, 518, 545, 589, 657. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3118, 1673, 1200, 1090, 820, 730.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -2.84 (s, 2H, pyrrole int.), 3.68 (s, 36H, O- $\text{CH}_3$ ), 7.15-7.24 (m, 8H, Ar), 8.01 (br, 4H, Ar), 8.17 (br, 4H, pyrrole), 9.11 (Ar), 102.6 (Ar-ring), 103.1 (methine), 122.7 (pyrrole), 132.1 (pyrrole), 142.33 (pyrrole), 158.9 (Ar), 159.6 (Ar), 162.41 (pyrrole). MALDI-TOF ( $m/z$ ): 974.37. Anal. calcd. for  $\text{C}_{56}\text{H}_{54}\text{N}_4\text{O}_{12}$ : C, 68.98; H, 5.58; N, 5.75. Found: C, 69.11; H, 5.73; N, 5.81%.

**Compound 4b:** Porphyrin **3b** (0.1 g, 0.1025 mmol) was added to 50 mL of dichloromethane at 100 °C until obtaining a homogenous solution.



Scheme 1

Later, it was cooled at 0 °C to add  $\text{BBr}_3$  (0.3082 g, 1.2306 mmol). The reaction was kept under constant stirring for 24 h. The product was dried in a rotary evaporator and later precipitated with a dichloromethane-hexane solution, obtaining the unprotected porphyrin-2, **4b** (Scheme 1). Color: Purple. Yield: 91%. UV/Vis ( $\text{CH}_3\text{OH}$ ,  $\lambda_{\text{max}}$ , nm): 220, 301, 418, 518, 545, 589, 657. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3638, 1673, 1200, 1010, 820, 730.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -2.84 (s, 2H, pyrrole int.), 5.89 (s, 12H, OH), 7.15-7.24 (m, 8H, Ar), 8.01 (br, 4H, Ar), 8.17 (br, 4H, pyrrole).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 91.04 (Ar), 91.78 (Ar), 102.6 (Ar-ring), 103.1 (methine), 122.7 (pyrrole), 132.1 (pyrrole), 142.33 (pyrrole), 158.9 (Ar), 159.6 (Ar), 162.41 (pyrrole). MALDI-TOF ( $m/z$ ): 806.19. Anal. calcd. for  $\text{C}_{44}\text{H}_{30}\text{N}_4\text{O}_{12}$ : C, 65.51; H, 3.75; N, 6.94. Found: C, 65.23; H, 4.13; N, 7.04%.

### 2.2.3. Synthesis of 0.5 generation dendrimers (6a, 6b)

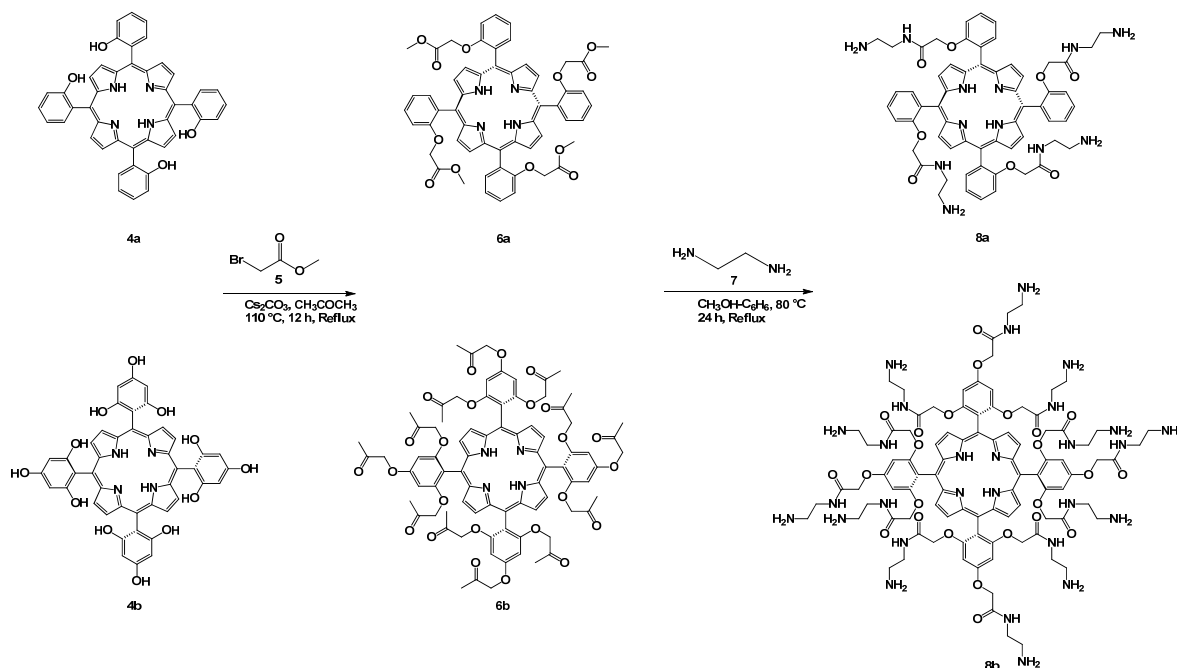
Separately, cesium carbonate (0.1920 g, 0.5893 mmol; 0.4846 g, 1.4874 mmol) and unprotected porphyrins **4a**, **4b** (0.1 g, 0.1473 mmol; 0.1 g, 0.1239 mmol) were added to 70 mL of acetone at 110 °C for 1 h. Finally, methyl bromo acetate (0.9 g, 0.5893 mmol; 0.2275 g, 1.4874 mmol) was added. The reaction was kept for 11 h more under constant stirring at the same temperature. The presence of the product was corroborated by thin layer chromatography and it was purified by filtering the solution in order to eliminate the cesium carbonate and later drying it in a rotary evaporator, finishing with a precipitation using a dichloromethane-hexane solution (1:1, v:v), obtaining the 0.5 generation dendrimer **6a**, **6b** as an intense purple powder (Scheme 2).

**Compound 6a:** Color: Metallic purple. Yield: 90%. UV/Vis ( $\text{CH}_3\text{OH}$ ,  $\lambda_{\text{max}}$ , nm): 220, 255, 421, 522, 568, 597, 679. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3448, 3314, 2986, 2851, 1754, 1603, 1509, 1223, 1168.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ ,  $\delta$ , ppm): -2.88 (s, 2H, pyrrole int.), 3.94 (s, 12H, O- $\text{CH}_3$ ), 4.91 (s, 8H,  $\text{CH}_2\text{-C=O}$ ) 7.24-7.28 (m, 8H, Ar), 8.09-8.10 (m, 8H, Ar), 8.12 (s, 8H, pyrrole).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ ,  $\delta$ , ppm): 51.9 (O- $\text{CH}_3$ ), 64.89 (O- $\text{C}^*\text{H}_2\text{-C=O}$ ), 99.3 (Ar-ring), 114.36 (Ar), 118.87 (pyrrole), 119.21 (Ar-ring), 120.64 (Ar), 127.67 (Ar), 142.13 (pyrrole), 155.7 (pyrrole), 157.82 (Ar), 162.31 (pyrrole), 170.12 (C=O). MALDI-TOF ( $m/z$ ): 966.31. Anal. calcd. for  $\text{C}_{56}\text{H}_{46}\text{N}_4\text{O}_{12}$ : C, 69.56; H, 4.79; N, 5.79. Found: C, 69.98; H, 4.81; N, 5.27%.

**Compound 6b:** Color: Metallic purple. Yield: 57%. UV/Vis ( $\text{CH}_3\text{OH}$ ,  $\lambda_{\text{max}}$ , nm): 209, 351, 418, 518, 555, 596, 653. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 2945, 2852, 1731, 1648, 1605, 1539, 1505, 1221, 1176.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -2.79 (s, 2H, pyrrole int.), 3.46 (br, 36H, O- $\text{CH}_3$ ), 4.79 (s, 24H,  $\text{CH}_2\text{-C=O}$ ), 7.18-7.37 (m, 8H, Ar), 8.16 (br, 4H, Ar), 8.85 (br, 4H, pyrrole).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 51.9 (O- $\text{CH}_3$ ), 64.89 (O- $\text{C}^*\text{H}_2\text{-C=O}$ ), 99.3 (Ar-ring), 114.36 (Ar), 118.87 (pyrrole), 119.21 (Ar-ring), 120.64 (Ar), 127.67 (Ar), 142.13 (pyrrole), 155.7 (pyrrole), 157.82 (Ar), 162.31 (pyrrole), 170.12 (C=O). MALDI-TOF ( $m/z$ ): 1481.34. Anal. calcd. for  $\text{C}_{80}\text{H}_{78}\text{N}_4\text{O}_{24}$ : C, 64.95; H, 5.31; N, 3.79. Found: C, 67.34; H, 5.77; N, 3.56.

### 2.2.4. Synthesis of generation 1 dendrimers (8a, 8b)

Separately, solutions adding ethylenediamine (0.024 g, 0.4136 mmol; 0.043 g, 0.7179 mmol) to 50 mL of a 1:1 (v:v) methanol:benzene mixture of compounds **6a** and **6b** (0.1 g, 0.1034 mmol; 0.1 g, 0.0598 mmol) were prepared at 80 °C with constant stirring for 36 h.



Scheme 2

The formation of the product was corroborated by thin layer chromatography and it was purified by drying the solution in a rotary evaporator and precipitating it with a dichloromethane:hexane (1:1, v:v) solution, obtaining the generation 1 dendrimer **8a**, **8b** as a purple powder (Scheme 2).

**Compound 8a**: Color: Purple. Yield: 94%. UV/Vis (CH<sub>3</sub>OH+CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>, nm): 233, 267, 433, 556, 596, 654, 716. FT-IR (KBr, ν, cm<sup>-1</sup>): 3360, 3316, 2948, 1671, 1603, 1504, 1239, 1169, 1059. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): -2.64 (s, 2H, pyrrole int.), 1.96 (t, 8H, NH<sub>2</sub>), 2.99 (br, 8H, CH<sup>\*</sup><sub>2</sub>-NH<sub>2</sub>), 3.54 (br, 8H, NH-CH<sub>2</sub><sup>\*</sup>), 4.01 (s, 8H, CH<sub>2</sub>-C=O), 7.17-7.21 (m, 8H, Ar), 7.37 (s, 8H, Ar), 8.04 (br, 4H, NH), 8.80 (br, 8H, pyrrole). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 38.74 (CH<sub>2</sub>-NH<sub>2</sub>), 48.97 (NH-CH<sub>2</sub>), 67.41 (C<sup>\*</sup>H<sub>2</sub>-C=O), 102.44 (methine), 116.72 (Ar), 118.97 (pyrrole), 122.14 (Ar), 123.41 (Ar-ring), 127.26 (Ar), 130.79 (Ar), 143.32 (pyrrole), 159.48 (Ar-ring), 163.16 (pyrrole), 173.49 (C=O). MALDI-TOF (*m/z*): 1080.88. Anal. calcd. for C<sub>60</sub>H<sub>62</sub>N<sub>12</sub>O<sub>8</sub>: C, 66.77; H, 5.79; N, 15.57. Found: C, 67.02; H, 5.76; N, 15.32%.

**Compound 8b**: Color: Purple. Yield: 34%. UV/Vis (CH<sub>3</sub>OH+CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>, nm): 204, 317, 418, 527, 561, 599, 687. FT-IR (KBr, ν, cm<sup>-1</sup>): 3249, 2945, 2871, 1657, 1602, 1532, 1503, 1224, 1173. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): -2.91 (s, 2H, pyrrole int.), 2.84 (br, 24H, NH<sub>2</sub>), 3.12 (s, 48H, NH-CH<sup>\*</sup><sub>2</sub>-CH<sup>\*</sup><sub>2</sub>-NH<sub>2</sub>), 4.82 (br, 24H, CH<sub>2</sub>-C=O), 7.43 (br, 8H, Ar), 8.12-8.21 (m, 8H, pyrrole), 8.84 (br, 12H, NH). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 38.74 (CH<sub>2</sub>-NH<sub>2</sub>), 48.97 (NH-CH<sub>2</sub>), 67.41 (C<sup>\*</sup>H<sub>2</sub>-C=O), 102.44 (methine), 116.72 (Ar), 118.97 (pyrrole), 122.14 (Ar), 123.41 (Ar-ring), 127.26 (Ar), 130.79 (Ar), 143.32 (pyrrole), 159.48 (Ar-ring), 163.16 (pyrrole), 173.49 (C=O). MALDI-TOF (*m/z*): 2007.95. Anal. calcd. for C<sub>92</sub>H<sub>126</sub>N<sub>28</sub>O<sub>24</sub>: C, 55.02; H, 6.32; N, 19.53. Found: C, 54.81; H, 6.64; N, 19.67%.

### 2.2.5. Synthesis of the functionalized generation 1 dendrimer (10a)

Generation 1 dendrimer **8a** (0.1 g, 0.0926 mmol) and ethyl 2-(2-chloroacetamido)-4-thiazole acetate (0.3715 mmol) were

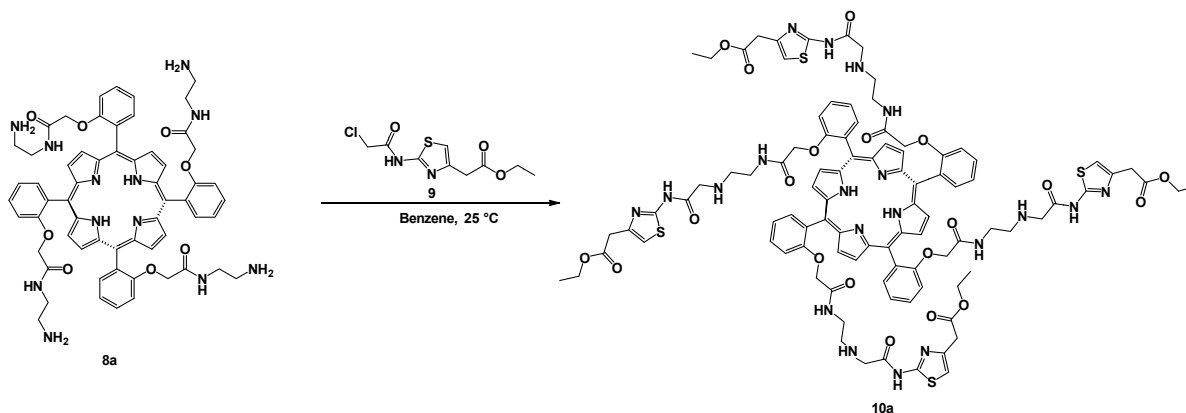
added to 20 mL of benzene. The reaction was cooled down at room temperature with constant stirring. The coupling was instantaneous, obtaining compound **10a** (Scheme 3). Color: Pink. Yield: 91%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>+DMSO-*d*<sub>6</sub>, δ, ppm): -2.74 (s, 2H, pyrrole int.), 1.28 (s, 12H, CH<sub>2</sub>-CH<sub>3</sub>), 2.58 (s, 8H, NH-CH<sub>2</sub>), 2.86 (br, 8H CH<sub>2</sub>-C=O), 3.68 (s, 16H, CH<sub>2</sub>-C=O, CH<sub>2</sub>-NH), 4.13 (s, 8H, CH<sub>2</sub>-CH<sub>3</sub>), 4.86 (s, 8H, CH<sub>2</sub>-C=O), 6.67 (s, 4H, thiazole ring), 6.82 (s, 4H, NH-thiazole ring), 7.31 (s, 8H, Ar), 7.51 (s, 8H, Ar), 7.97 (s, 8H, pyrrole), 9.81 (br, 8H, NH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>+DMSO-*d*<sub>6</sub>, δ, ppm): 13.59 (CH<sub>2</sub>-CH<sub>3</sub>), 36.6 (CH<sub>2</sub>-C=O), 39.77 (NH-CH<sub>2</sub>), 40.05 (CH<sub>2</sub>-NH), 51.4 (CH<sub>2</sub>-C=O), 60.2 (CH<sub>2</sub>-CH<sub>3</sub>), 66 (CH<sub>2</sub>-C=O), 112.4 (methine), 122 (CH, ring-CH<sub>2</sub>), 128 (Ar), 134.6 (CH=CH, ring), 143.8 (pyrrole), 145 (Ar), 151 (pyrrole) 157.03 (C-O), 161 (N-CH-S, ring), 164.24 (C=O), 169.55 (C=O), 173 (C=O). MALDI-TOF (*m/z*): 1997.67. Anal. calcd. for C<sub>97</sub>H<sub>104</sub>N<sub>20</sub>O<sub>20</sub>S<sub>4</sub>: C, 58.30; H, 5.25; N, 14.02. Found: C, 58.45; H, 5.41; N, 13.71%.

## 3. Results and discussion

### 3.1. Synthesis

Porphyrin-**3a** and **3b** were synthesized by a condensation reaction between pyrrole (**1**) and 2-methoxybenzaldehyde (**2a**) and 2,4,6-trimethoxybenzaldehyde (**2b**). The reaction was performed for 35 min at 80 °C by means of a microwave reactor Monowave 300. Compounds **3a** and **3b** were obtained as very intense purple powders with an approximate yield of 3%, Scheme 1.

The obtained porphyrins (compounds **3a** and **3b**) were characterized firstly by UV-vis spectrometry, finding five typical porphyrin bands: a high intensity band known as the Soret band appears at 420 nm and four low intensity bands, known as the Q bands, are located between 500 and 700 nm; at 200 and 230 nm, two bands can be seen, which correspond to the aliphatic chains for both compounds. The structures were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, where the most important signals for internal protons in the porphyrine group appeared at δ -2.82 ppm for compound **3a**, and at δ -2.84 ppm for compound **3b**.



Scheme 3

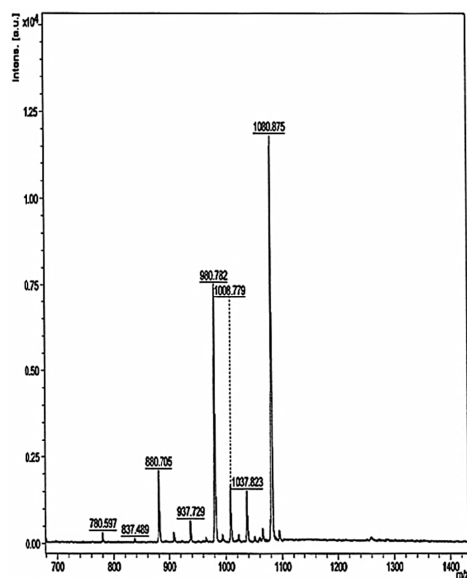


Figure 1. MALDI-TOF spectrum of compound 8a.

After performing the deprotection reaction using  $\text{BBr}_3$  and obtaining the unprotected porphyrins, compounds **4a** and **4b** continued building the macromolecules (dendrimers), Scheme 2.

The dendrimer structures were also confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, and MALDI-TOF mass spectrometry. It was found that all the dendrimers had an expected molecular weight. The MALDI-TOF mass spectrum of compound **8a** is shown in Figure 1.

Compound **8b** was characterized by  $^1\text{H}$  NMR (Figure 2), where the following representative molecule signals were observed. A broad signal at  $\delta$  -2.75 ppm corresponds to internal pyrrolic N-H protons inside the macrocycle; a multiplet at  $\delta$  8.12-8.21 ppm corresponds to eight protons of the porphyrin ring. A broad signal at  $\delta$  2.84 ppm corresponds to twenty-four protons of primary amines ( $\text{NH}_2$ ) in the periphery of the dendrimer; the singlet at  $\delta$  3.12 ppm corresponds to forty eight protons of the  $\text{CH}_2\text{-CH}_2$  chains between the amine groups. A broad signal at  $\delta$  4.82 ppm is assigned to twenty-four  $\text{CH}_2$  protons linked to the carbonyl group. For eight aromatic protons, a broad signal is located at  $\delta$  7.43 ppm. Finally, a broad signal at  $\delta$  8.84 ppm is assigned to twelve protons of a secondary amine (NH).

In order to increase the number of active centers inside the dendrimer branches to form bonds with metals, new heterocyclic rings with N and S elements were introduced, Scheme 3.

The present work was aimed at studying the formation process of the porphyrine-dendrimer-metal complex, Scheme 4. In order to reach this goal, different salts soluble in aqueous solutions such as  $\text{CoCl}_2$ ,  $\text{CuSO}_4$ ,  $\text{NiCl}_2$  and  $\text{AgC}_2\text{H}_3\text{O}_2$  with concentrations between 2 and 5 ppm were used. In most cases, these negligible concentrations are hard to be removed from water solutions. The removing process was carried out under neutral pH (6.1-7.8) conditions and at room temperature. After using a nylon membrane with 0.45  $\mu\text{m}$  pores for the filtration process, the oxidation states of the formed species were obtained by the X-ray photoelectron spectroscopy technique.

The X-ray photoelectron spectroscopy (XPS) allowed to perform a surface-sensitive-quantitative-spectroscopic and elemental analysis. The XPS technique is widely used to generate an empirical formula because it readily yields excellent quantitative accuracy from homogeneous solid-state materials.

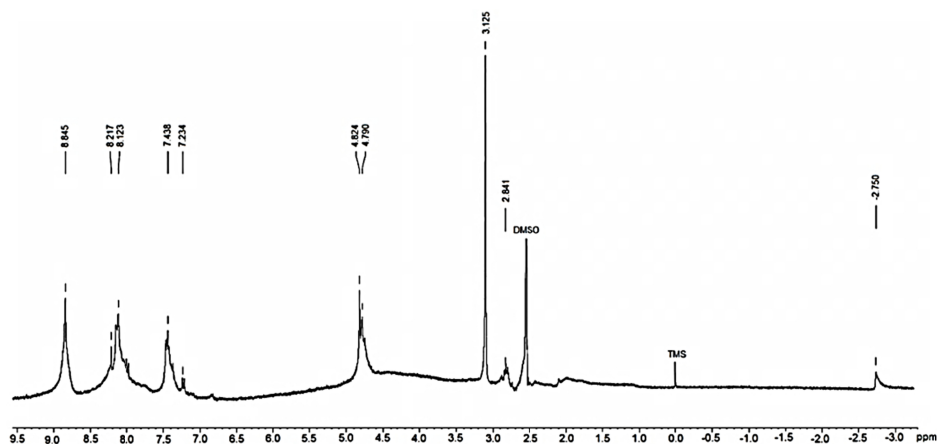
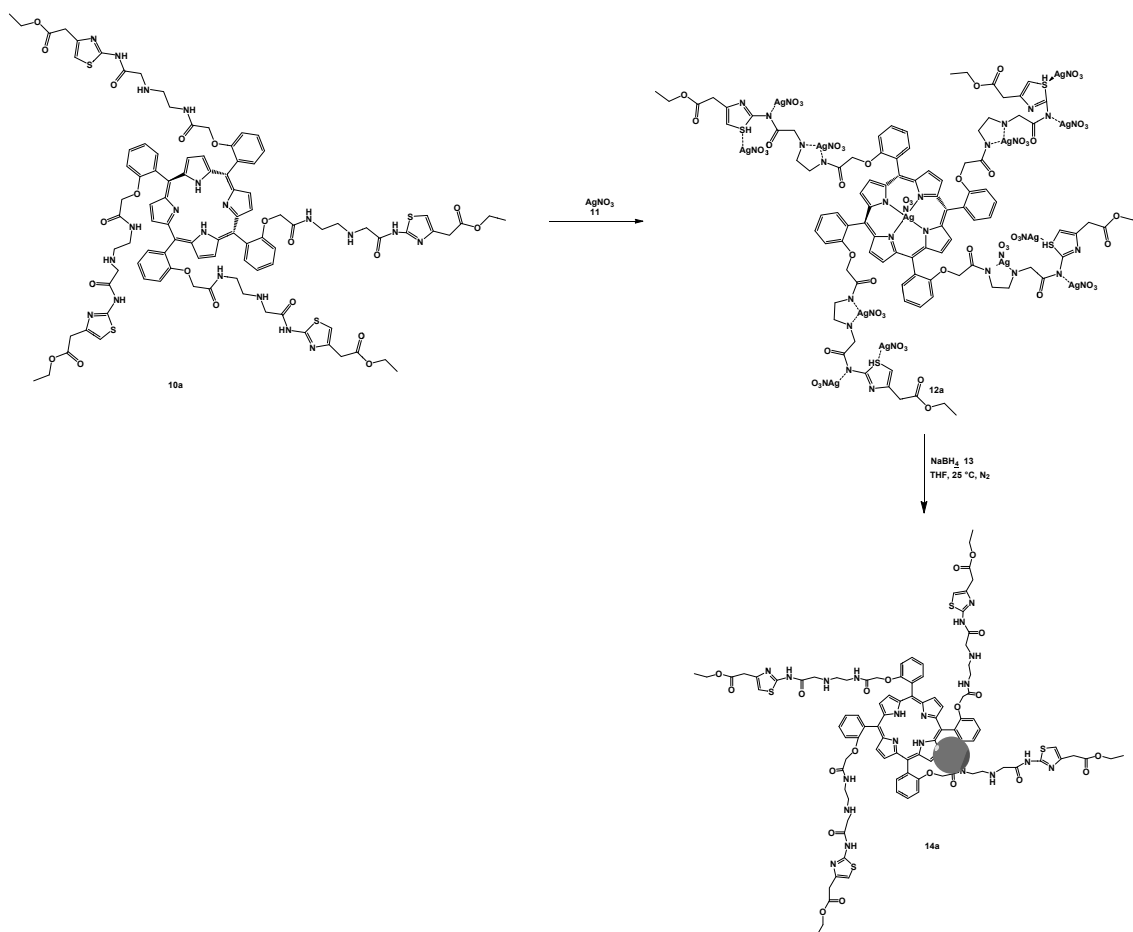


Figure 2.  $^1\text{H}$  NMR spectrum of compound **8b**.



Scheme 4

In our case, through the analysis of high resolution XPS Ag peaks (Figure 3), it was corroborated that  $\text{NaBH}_4$  was able to reduce the cation to its metallic state, where the doublet at 368.18 and 374.19 eV corresponds to  $\text{Ag}^0$  present at 86.88%. An Ag-O doublet at 367.34 and 373.27 eV was also observed at 13.12%.

#### 4. Conclusion

New porphyrins were successfully synthesized by the microwave method, which was corroborated by UV-vis spectrophotometry, FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and mass spectrometry.

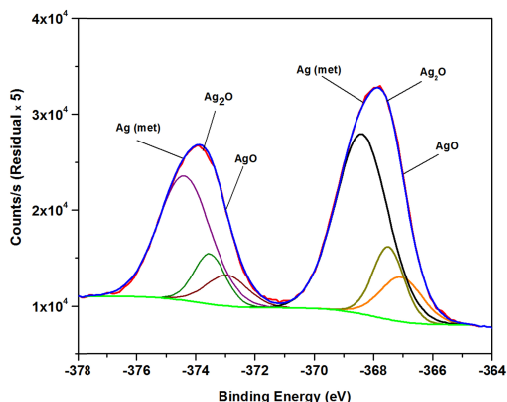


Figure 3. X-ray photoelectron spectra of compound **14a** with  $\text{Ag}^0$ .

The microwave-assisted synthesis of porphyrins allowed to achieve increasing reaction yields as well as both shorter reaction times and lower solvent amounts. The synthesis of four new dendrimers with PAMAM ramifications from Porphyrin-**3a** as center was successful, giving a first-generation dendrimer with a functionalized periphery, achieving very good yields through controlled reactions at each stage. Furthermore, two new dendrimers with PAMAM ramifications from a Porphyrin-**3b** center were synthesized successfully. The chemical reduction performed by the dendrimer-metal complex was verified by means of XPS, finding that Ag was reduced at 86.88% of  $\text{Ag}^0$ , and also for Ni (18.94%), Co (29.4%) and Cu (26.4%). Thanks to the dendrimer-metal complexes, it was possible to carry out the chemical reduction of the aforesaid metals in aqueous phase and with pH values close to neutrality, where the active periphery with amine functional groups was capable of forming bonds with the metal cations. Ag was the metal that was found in higher reduced amounts since this is a noble metal and it is not oxidized easily with respect to Ni, Cu and Co, which were found in proportions below 30% of the metal phase. Porphyrin is a determining molecule that has the capacity of forming complexes with metal cations, which along with the dendritic branches is capable of interacting with metal cations thanks to its nucleophilic character.

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