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## Synthesis and Photophysical Properties of Novel Pyrene-Metalloporphyrin Dendritic Systems

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#### Abstract

A novel series of dendronized porphyrins bearing pyrene units in the periphery (Porph-O- $G_n$ ) and their metal complexes (M-[Porph-O- $G_n$ ]) are reported. The pyrene-containing Frechet-type dendrons up to first generation were synthesized and further reacted with 5-phenol-10,15,20-triphenylporphyrin *via* an esterification reaction to afford the desired pyrene-labeled dendronized porphyrins. Later, these compounds were used as ligands to produce the corresponding complexes of Zn<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup> and Mn<sup>3+</sup>. With the compounds in hand, the optical and photophysical properties of the dendritic metalloporphyrins were studied by absorption and fluorescence spectroscopies. The quantum yields, Förster radius and efficiency of energy transfer were determined and discussed in function of the structure and the donor-acceptor distances, finding an efficient energy transfer from the pyrene moiety to the metallated porphyrin core in each case.

**Keywords**: Dendrimers, Pyrene substituents, Metalloporphyrin, Photophysical properties, Fluorescence.

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#### 1. Introduction

Dendrimers have represented a motif of great importance and focus of multiple studies during the last decades due to their notable physical and chemical properties.<sup>1–3</sup> They display promising applications in various fields of materials science ranging from the elaboration of electroactive and photoactive devices to biological applications for the administration and release of drugs as well as their use as catalysts in potentially relevant organic transformations.<sup>4–11</sup> Particularly relevant results the field of photoactive dendrimers, where their photophysical properties can be modulated by careful design of their architectures. The photoactive units might be located either at the core, in the dendritic building units or at the periphery, giving rise to different photophysical phenomena, such as fluorescence resonance energy transfer (FRET) and charge transfer (CT). Being these processes very important in the design and development of photovoltaic devices.<sup>12–17</sup>

One of the most commonly used chromophores in dendritic and polymeric structures is the Pyrene due to its unique and outstanding optical and luminescent properties.<sup>18–25</sup> Moreover, it exhibits the ability to form excimers when its local concentration increases.<sup>25,26</sup> Thus, there are many reports of dendritic and polymeric architectures incorporating this chromophore and has also been covalently linked to diverse acceptor groups.<sup>27–31</sup>

On the other hand, the porphyrin chromophore is among the most investigated acceptor in dendritic structures due to its versatility and its use in different fields such as photodynamic therapy, catalysis, non-linear optics and fluorescent switches.<sup>32–39</sup> In addition, one of the most important applications of this chromophore is the design of solar cells based on molecular systems mimicking to those involved in photosynthesis, acting as sensitizers of light absorption.<sup>40,41</sup> Thus, a large variety of dendritic structures with donor-

acceptor groups containing porphyrin have been reported,<sup>42–44</sup> some of which have been contributions of our research group, focusing on the study of dendritic structures based on the pyrene-porphyrin pair of chromophores for energy transfer purposes leading to astonishing energy transfer efficiencies close to 100%.<sup>45–47</sup>

Natural porphyrin derivatives with important biological activity for dioxygen transport and photosynthesis, are based on metalloporphyrin moieties. Complexes of iron, magnesium and cobalt are found in heme, chlorophyll and vitamin B<sub>12</sub>, respectively.<sup>48,49</sup> Artificial metalloporphyrin complexes such as meso substituted porphyrins are easy to synthesize and modify. The main feature of these systems is that they exhibit a strong absorption band in the UV-vis spectrum (Soret band) in the blue region as well as low intensity Q bands near the red region.<sup>50</sup> Changes in the absorption spectra are observed depending on the metal ion coordinated to the porphyrin ligand.<sup>51</sup> It is due to these photophysical as well as to their redox properties that metalloporphyrins have found applications in analytical chemistry and catalysis in oxidation reactions as well as building blocks in the production of metal organic framework.<sup>52–58</sup>

Thus, in this work, we studied the effect of the metallation of some porphyrins on the energy transfer from a pyrene moiety. Here, Zn, Cu, Mg, and Mn ions were complexed to pyrene-labeled dendronized porphyrins. Since metallation strongly affects the optical and electrochemical properties of the porphyrin chromophore, the UV-vis and fluorescence properties of all the compounds was studied.

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#### 2. Experimental Section

#### 2.1 General Notes

For the synthesis of the porphyrins, dendrons of zero and first generation  $Py_1G_0Br$ and Py<sub>2</sub>G<sub>1</sub>Br were used.<sup>46,59</sup> All the reagents were purchased from Aldrich and used as received. The solvents employed were purified by simple distillation. The purifications by means of chromatographic columns were carried out in neutral alumina or silica gel packed in glass columns, and the eluting solvents for the purifications were determined by thin layer chromatography. The NMR spectra were recorded on a Bruker Avance 400 MHz, operating at 400 and 100 MHz for <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}, respectively. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) measurements were conducted with a Bruker Daltonics Flex Analysis spectrometer. Elemental analyses were done on a Flash 2000 instrument from Thermo Scientific. Absorption spectra of the different compounds were scanned on a Unicam UV300 spectrophotometer. The absorption spectra were acquired with a 1 cm path length quartz cell to determine the molar absorption coefficient of the constructs at the Soret band and at 344 nm for the pyrene band, respectively. The steady-state fluorescence spectra were recorded in a Fluorolog3 Horiba spectrofluorometer with Xenon lamp as light source. The slit widths in the excitation and emission monochromators were adjusted to 1 and 1 nm, respectively. The concentration for all the compounds was  $1.0 \times 10^{-7}$  and  $1.3 \times 10^{-6}$  M for the porphyrin and pyrene respectively. Time-resolved fluorescence measurements were performed on Horiba instrument using Time Correlated Single Photon Counting (TCSPC) and equipped with a NanoLED-350 nm for pyrene excitation and a NanoLED-425 nm for porphyrin excitation. All decays were acquired using a time per channel of 219 ps or 55 ps depending on the range of the

measured lifetime. The instrument response function (IRF) was measured with a LUDOX solution in water.

## 2.2 Synthetic procedures for the free-base monosubstituted porphyrins 2.2.1 Synthesis of 5,10,15,20-tetraphenylporphyrin (TPP) (1) and 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (Porph-OH) (2)

Compounds **1** and **2** were synthesized according to the method published by our research group<sup>60,61</sup> following the general procedure reported by Lindsey<sup>62</sup> for the synthesis of porphyrins. Symmetric porphyrin **1** was obtained as a purple solid (1.99 g, 17%) and asymmetric porphyrin **2** was obtained also as a purple solid (1.66 g, 14%). **TPP (1)**  $\delta$  <sup>1</sup>H (400 MHz; CDCl<sub>3</sub>) –2.76 (2H, s, NH), 7.72-7.79 (12H, m, H1, H3), 8.22 (8H, d, J = 7.6 Hz, H2), 8.86 (8 H, s, H7).  $\delta$  <sup>13</sup>C (100 MHz; CDCl<sub>3</sub>) 76.7, 77.0, 77.4, 120.2, 126.7, 127.7, 134.6, 142.3. UV-Vis:  $\lambda$ max (THF) / nm 418  $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 451,000), 513, 548, 593 and 649 nm. Analysis Elemental: Found: C, 85.91; N, 8.99; H, 4.86. C<sub>44</sub>H<sub>30</sub>N<sub>4</sub>: requires C, 85.97; N, 9.11; H, 4.92%. **Porph-OH (2)**  $\delta$  <sup>1</sup>H (400 MHz; CDCl<sub>3</sub>) –2.79 (2H, s, NH), 7.20 (2H, d, J = 8.4 Hz, H3'), 7.74-7.79 (9H, m, H1, H2), 8.07 (2H, d, J = 8.6 Hz, H2'), 8.20-8.23 (6H, m, H3) 8.84-8.89 (8H, m, H7, H8, H12, H13).  $\delta$  <sup>13</sup>C (100 MHz; CDCl<sub>3</sub>) 112.9, 120.1, 120.2, 126.8, 127.8, 129.3, 134.7, 134.8, 135.6, 142.3, 158.7. UV-Vis:  $\lambda$ max (THF) / nm 418 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 451 000), 513, 548, 593 and 649 nm.

## 2.2.2 Synthesis of 5,10,15-triphenyl-20-(4-(4-(pyren-1-yl)butoxy)phenyl) porphyrin (Porph-0-PyG<sub>0</sub>) (3)

 $Py_1G_0Br$  (96 mg, 0.28 mmol) and Porph-OH (180 mg, 0.28 mmol) were dissolved in 100 mL anhydrous acetone, then K<sub>2</sub>CO<sub>3</sub> (197 mg, 1.43 mmol) and 18-ether crown-6 in

catalytic amounts were added to the reaction mixture and allowed to reflux for 72 hours under inert atmosphere. After this time, the reaction mixture was cooled down to room temperature and concentrated under vacuum. The crude product was dissolved in dichloromethane and washed with water. The organic phase was concentrated at reduced pressure and the crude product purified by flash column chromatography (SiO<sub>2</sub>, Hexane/CH<sub>2</sub>Cl<sub>2</sub>: 9/1 then CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9.5/0.5). The final product was obtained as a purple solid (245mg, 96%). δ <sup>1</sup>H (400 MHz; CDCl<sub>3</sub>) -2.74 (2H, s, NH), 2.18-2.31 (4H, m, H6', H7'), 3.59 (2H, t, J= 7.4 Hz, H8'), 4.35 (2H, t, J= 6.0 Hz, H5'), 7.29 (2H, d, J = 7.3 Hz, H3'), 7.76-7.83 (9H, m, H1, H3), 8.0-8.09 (4H, m, Hpy), 8.14 (2H, d, J = 8.1 Hz, H2'), 8.19-8.26 (10H, m, 4Hpy, 6H2), 8.43 (1H, d, J = 8.4 Hz, Hpy), 8.85-8.91 (8H, m, H7, H8, H12, H13). δ <sup>13</sup>C (100 MHz; CDCl<sub>3</sub>) 28.4, 29.4, 33.3, 68.1, 76.7, 77.1, 77.3, 112.7, 119.9, 120.0, 120.1, 123.4, 124.7, 124.8, 124.9, 125.1, 125.2, 125.8, 126.7, 127.3, 127.5, 127.7, 128.7, 129.9, 130.9, 131.4, 134.4, 134.5, 135.6, 136.6, 142.2, 158.9. MS (ESI) m/z calculated for  $C_{64}H_{46}N_4O$  [M]<sup>+</sup>: 887.10; found 887.37). UV-Vis:  $\lambda$ max (THF) / nm 344, 417, ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 63 000, 467 000), 512, 549, 592 and 648 nm. Analysis Elemental: Found: C, 86.39; N, 6.35; H, 5.29. C<sub>64</sub>H<sub>46</sub>N<sub>4</sub>O: requires C, 86.65; N, 6.32; H, 5.23%. R<sub>f</sub>  $(\text{Hexane/CH}_2\text{Cl}_2: 1/1) = 0.57.$ 

### 2.2.3 Synthesis of 5-(4-((3,5-bis(4-(pyren-1-yl)butoxy)benzyl)oxy)phenyl)-10,15,20triphenylporphyrin (Porph-0-Py<sub>2</sub>G<sub>1</sub>) (4)

 $Py_2G_1Br$  (113 mg, 0.16 mmol) and Porph-OH (100 mg, 0.16 mmol) were dissolved in 100 mL of anhydrous DMF, then  $K_2CO_3$  (109 mg, 0.79 mmol) and 18-crown-6 ether were added in catalytic amounts to the reaction mixture and allowed to reflux for 72 hours under inert atmosphere. After this time, the resulting reaction mixture was cooled to room

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temperature and concentrated under vacuum. The crude product was dissolved in dichloromethane and washed with water. The organic phase was concentrated at reduced pressure and the product purified by column chromatography (SiO<sub>2</sub>, Hexane/CH<sub>2</sub>Cl<sub>2</sub>: 8/2then CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1). The product was obtained as a purple fluffy solid (180 mg, 90%).  $\delta^{-1}$ H (400 MHz; CDCl<sub>3</sub>) -2.52 (2H, s, NH), 2.09 (8H, m, H10', H11'), 3.45 (4H, t, J =7.6 Hz, H12'), 4.13 (4H, t, J = 6.2 Hz, H9'), 5.18 (2H, s, H5'), 6.63 (1H, t, J = 2.1 Hz, H8'), 6.83 (2H, d, J = 2.1 Hz, H7'), 7.38 (2H, d, J = 8.6 Hz, H3'), 7.83-7.88 (9H, m, H1, H3), 7.91 (2H, d, J = 7.8 Hz, Hpy), 7.96-8.17 (14H, m, Hpy), 8.22 (2H, d, J = 8.6 Hz, H2'), 8.33  $(2H, d, J = 9.3 \text{ Hz}, \text{Hpy}), 8.36-8.39 (6H, m, H2), 8.99-9.07 (8H, m, H7, H8, H12, H13).\delta$ <sup>13</sup>C (100 MHz; CDCl<sub>3</sub>) 28.3, 29.2, 33.2, 67.9, 70.3, 76.7, 77, 77.3, 101.08, 106.1, 113.2, 120, 120.1, 123.4, 124.7, 124.83, 124.86, 125, 125.1, 125.8, 126.6, 126.7, 127.2, 127.5, 127.7, 128.6, 129.8, 130.9, 131.4, 134.6, 134.8, 135.6, 136.5, 139.3, 142.2, 160.5. MS (MALDI-TOF) m/z calculated for  $C_{91}H_{68}N_4O_3$  [M]<sup>+</sup>: 1265.57; Found 1265.55. UV-Vis:  $\lambda$ max (THF) / nm 344, 418, ( $\epsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 101 000, 456 000), 512, 549, 592 and 648 nm. Analysis Elemental: Found: C, 64.34; N, 4.41; H, 5.45. C<sub>91</sub>H<sub>68</sub>N<sub>4</sub>O<sub>3</sub>: requires C, 86.36; N, 4.43; H, 5.42%.  $R_f$  (Hexane/CH<sub>2</sub>Cl<sub>2</sub>: 4/6) = 0.4.

#### 2.3 Synthetic procedures for the monosubstituted metalloporphyrins

#### 2.3.1 General methodologies for the metallation reactions

A. The corresponding porphyrin and the metal salt were dissolved in DMF under inert atmosphere and heated to 110°C. The reaction was monitored by UV-Vis spectroscopy. It was observed that the reaction was finished after 3 hours. The purification of the metallated porphyrins was carried out by precipitation using a mixture dichloromethane/hexane. Page 9 of 39

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**B.** The corresponding porphyrin and the metal salt were dissolved in DMF under inert atmosphere and heated to reflux. The reaction was monitored by UV-Vis spectroscopy. It was observed that the reaction was finished after 12 hours. The purification of the metallated porphyrins was carried out by precipitation using a mixture dichloromethane/hexane.

#### 2.3.2 Synthesis M-[TPP] series

**Zn-TPP (1a): TPP** (300 mg, 0.48 mmol) and  $Zn(CH_3CO_2)_2 \cdot 2H_2O$  (448 mg, 2.44 mmol), following the metallation method A. Compound **1a** was obtained as a light purple solid (147mg, 45%).  $\delta$  <sup>1</sup>H (400 MHz; CDCl<sub>3</sub>) 7.72-7.79 (12H, m), 8.21-8.24 (8H, m), 8.95 (8 H, m). MS (MALDI-TOF) m/z calculated for C<sub>44</sub>H<sub>28</sub>ZnN<sub>4</sub> [M+H]<sup>+</sup>: 678.12; Found 678.16. UV-Vis:  $\lambda$ max (THF) / nm 423 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 661,500), 556 and 593 nm. Analysis Elemental: Found: C, 77.86 ; N, 8.23; H, 4.08. C<sub>44</sub>H<sub>28</sub>ZnN<sub>4</sub>: requires C, 77.93; N, 8.26; H, 4.16%.

**Cu-TPP (1b): TPP** (200 mg, 0.33 mmol) and CuCl<sub>2</sub>·4H<sub>2</sub>O (438 mg, 3.26 mmol), following the metallation method A. Compound **1b** was obtained as a dark purple solid (161mg, 72%). MS (MALDI-TOF) m/z calculated for C<sub>44</sub>H<sub>28</sub>CuN<sub>4</sub> [M]<sup>+</sup>: 676.27; Found 676.25. UV-Vis:  $\lambda$ max (THF) / nm 415 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 439 500), 540 nm. Analysis Elemental: Found: C, 78.13; N, 8.16; H, 4.09. C<sub>44</sub>H<sub>28</sub>CuN<sub>4</sub>: requires C, 78.15; N, 8.12; H, 4.17%.

**Mg-TPP (1c): TPP** (300 mg, 0.48 mmol) and MgCl<sub>2</sub>·4H<sub>2</sub>O <sup>48</sup> (2094 mg, 9.77 mmol) in basic medium using triethylamine (988 mg, 1.36 mL, 9.768 mmol), following the metallation method B. Compound **1c** was obtained as a green solid (172mg, 56%).  $\delta$  <sup>1</sup>H (400 MHz; CDCl<sub>3</sub>) 7.71-7.75 (12H, m), 8.21-8.24 (8H, m), 8.84 (8 H, m). MS

(MALDI-TOF) m/z calculated for  $C_{44}H_{28}MgN_4$  [M]<sup>+</sup>: 637.03; Found 637.02. UV-Vis:  $\lambda max$  (THF) / nm 429 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 552 500), 571 and 613 nm. Analysis Elemental: Found: C, 82.93 ; N, 8.74; H, 4.38.  $C_{44}H_{28}MgN_4$ : requires C, 82.96; N, 8.80; H, 4.43%.

**MnCl-TPP (1d):** TPP (300 mg, 0.48 mmol) and MnCl<sub>2</sub>·4H<sub>2</sub>O (483 mg, 2.44 mmol), following the metallation method B. Compound **1d** was obtained as a green solid (153 mg, 45%). MS (ESI) m/z calculated for  $C_{44}H_{28}MnN_4Cl$  [M-Cl]<sup>+</sup>: 667.17; Found 667.17. UV-Vis:  $\lambda$ max (THF) / nm 369, 396, 476 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 35 000, 31 500, 69 000), 586 and 623 nm. Analysis Elemental: Found: C, 75.14; N, 7.92; H, 4.00.  $C_{44}H_{28}MnN_4Cl$ : requires C, 75.16; N, 6.89; H, 4.01%.

#### 2.3.3 Synthesis M[Porph-O-Py G<sub>0</sub>] series

Zn-Porph-O-PyG<sub>0</sub> (**3**a): Porph-O-PyG<sub>0</sub> (150)0.17 mmol) mg, and  $Zn(CH_3CO_2)_2 \cdot 2H_2O$  (117 mg, 0.85 mmol), following the metallation method A. Compound **3a** was obtained as a light purple solid (162 mg, 84%).  $\delta^{-1}$ H (400 MHz; CDCl<sub>3</sub>) 2.17-2.27 (4H, m), 3.54-3.61 (2H, m), 4.31-4.35 (2H, m), 7.26 (2H, m), 7.73-7.81 (9H, m), 8.05-8.12 (6H, m), 8.21-8.23 (9H, m), 8.39-8.43 (1H, m), 8.97-8.94 (8H, m). MS (MALDI-TOF) m/z calculated for  $C_{64}H_{44}ZnN_4O$  [M+H]<sup>+</sup>: 950.46; Found 951.92. UV-Vis:  $\lambda$ max (THF) / nm 344, 424, ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 55 000, 579 000), 556 and 593 nm. Analysis Elemental: Found: C, 80.85; N, 5.86; H, 4.64 %. C<sub>64</sub>H<sub>44</sub>ZnN<sub>4</sub>O: requires C, 80.88; N, 5.89; H, 4.67%.

**Cu-Porph-O-PyG<sub>0</sub> (3b):** Porph-O-PyG<sub>0</sub> (150 mg, 0.17 mmol) and CuCl<sub>2</sub>·4H<sub>2</sub>O (227 mg, 1.69 mmol), following the metallation method A. Product **3b** was obtained as a dark purple solid (130 mg, 80%). MS (MALDI-TOF) m/z calculated for  $C_{64}H_{44}CuN_4O$ 

 $[M+H]^+$ : 948.60; Found 948.92. UV-Vis:  $\lambda max$  (THF) / nm 344, 416, ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 50 000, 495 000), 540 nm. Analysis Elemental: Found: C, 80.97; N, 5.87; H, 4.64. C<sub>64</sub>H<sub>44</sub>CuN<sub>4</sub>O: requires C, 81.03; N, 5.91; H, 4.68 %.

**Mg-Porph-O-PyG**<sup>0</sup> (3c): Porph-O-PyG<sub>0</sub> (300 mg, 0.34 mmol) and MgCl<sub>2</sub>·4H<sub>2</sub>O (1451 mg, 6.77 mmol) in basic medium using triethylamine (685 mg, 0.94 mL, 6.77 mmol), following the metallation method B. Product **3c** was obtained as a green solid (202 mg, 65%). δ <sup>1</sup>H (400 MHz; CDCl<sub>3</sub>) 1.70-2.16 (4H, m), 3.52-3.56 (2H, m), 4.24-4.29 (2H, m), 7.27 (2H, m), 7.70-7.76 (9H, m), 7.97-8.11 (6H, m), 8.15-8.20 (9H, m), 8.38-8.41 (1H, m), 8.84-8.88 (8H, m). MS (MALDI-TOF) m/z calculated for C<sub>64</sub>H<sub>44</sub>MgN<sub>4</sub>O [M]<sup>+</sup>: 909.36; Found 909.88. UV-Vis:  $\lambda$ max (THF) / nm 344, 430, ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 48 000, 453 000), 571 and 613 nm. Analysis Elemental: Found: C, 84.48 ; N, 6.12; H, 4.83. C<sub>64</sub>H<sub>44</sub>MgN<sub>4</sub>O: requires C, 84.53; N, 6.16; H, 4.88%.

**MnCl-Porph-O-PyG<sub>0</sub> (3d):** Porph-O-PyG<sub>0</sub> (300 mg, 0.34 mmol) and MnCl<sub>2</sub>·4H<sub>2</sub>O (335 mg, 1.69 mmol), following the metallation methodology B. Product **3d** was obtained as a green solid (132 mg, 40%). MS (ESI) m/z calculated for C<sub>64</sub>H<sub>44</sub>MnN<sub>4</sub>OCl [M-Cl]<sup>+</sup>: 940.02; Found 939.29. UV-Vis:  $\lambda$ max (THF) / nm 344, 369, 396, 474 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 79 000, 50 000, 50 500, 96 500), 580 and 623 nm. Analysis Elemental: Found: C, 78.75; N, 5.68; H, 4.57. C<sub>64</sub>H<sub>44</sub>MnN<sub>4</sub>OCl: requires C, 78.80; N, 5.74; H, 4.55%.

#### 2.3.4 Synthesis M[Porph-O-Py<sub>2</sub> G<sub>1</sub>] series

**Zn-Porph-O-Py<sub>2</sub>G<sub>1</sub> (4a):** Porph-O-Py<sub>2</sub>G<sub>1</sub> (50 mg, 0.039 mmol) and  $Zn(CH_3CO_2)_2 \cdot 2H_2O$  (55 mg, 0.395 mmol), following the metallation method A. The metallated porphyrin product was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> then CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1). Compound **4a** was obtained as a purple solid (42 mg, 81%).  $\delta$  <sup>1</sup>H (400

MHz; CDCl<sub>3</sub>) 1.97-2.08 (8H, m), 3.39-3.43 (4H, m), 4.03-4.07 (4H, m), 5.21-5.29 (2H, m), 6.42-6.46 (1H, m), 6.71-6.72 (2H, m), 7.69-7.77 (2H, m), 7.74-8.07 (18H, m), 8.10 (2H, m), 8.19-8.27 (6H, m), 8.90-9.96 (8H, m). MS (MALDI-TOF) m/z calculated for  $C_{91}H_{66}ZnN_4O_3$  [M+H]<sup>+</sup>: 1,328.90; Found 1,330.55. UV-Vis:  $\lambda max$  (THF) / nm 344, 424 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 99 000, 614 500), 556 and 593 nm. Analysis Elemental: Found: C, 82.21; N, 4.18; H, 4.17.  $C_{91}H_{66}ZnN_4O_3$ : requires C, 82.25; N, 4.22; H, 5.01%.

**Cu-Porph-O-Py<sub>2</sub>G<sub>1</sub> (4b):** Porph-O-Py<sub>2</sub>G<sub>1</sub> (50 mg, 0.039 mmol) and CuCl<sub>2</sub>·4H<sub>2</sub>O (106 mg, 0.7908 mmol), following the metallation method A. The metallated porphyrin product was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, Hexane/CH<sub>2</sub>Cl<sub>2</sub>: 8/2 then Hexane/CH<sub>2</sub>Cl<sub>2</sub>: 1/1). Compound **4b** was obtained as a red solid (41 mg, 78%). MS (MALDI-TOF) m/z calculated for C<sub>91</sub>H<sub>66</sub>CuN<sub>4</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 1,327.07; Found 1,329.61. UV-Vis:  $\lambda$ max (THF) / nm 344, 416 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 83 000, 434 500), 540 nm. Analysis Elemental: Found: C, 82.46; N, 4.24; H, 5.04. C<sub>91</sub>H<sub>66</sub>CuN<sub>4</sub>O<sub>3</sub>: requires C, 82.36; N, 4.22; H, 5.01%.

**Mg-Porph-O-Py<sub>2</sub>G<sub>1</sub> (4c):** Porph-O-Py<sub>2</sub>G<sub>1</sub> (50 mg, 0.039 mmol) and MgCl<sub>2</sub>·4H<sub>2</sub>O (254 mg, 1.186 mmol) in basic medium triethylamine (120 mg, 0.165 mL, 1.186 mmol). following the metallation method B. The metallated porphyrin product was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> then CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9.5/0.5). Compound **4c** was obtained as a green solid (20 mg, 40%).  $\delta$  <sup>1</sup>H (400 MHz; CDCl<sub>3</sub>) 1.93-2.09 (8H, m), 3.38-3.43 (4H, m), 4.00-4.06 (4H, m), 5.13-5.19 (2H, m), 6.43-6.45 (1H, m), 6.70-6.71 (2H, m), 7.68-7.77 (2H, m), 7.69-8.08 (18H, m), 8.11 (2H, m), 8.18-8.28 (6H, m), 8.81-9.96 (8H, m). MS (MALDI-TOF) m/z calculated for C<sub>91</sub>H<sub>66</sub>MgN<sub>4</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 1,287.83; Found 1,289.71. UV-Vis:  $\lambda$ max (THF) / nm 344, 430 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 83 500, 506 000), 571

and 613 nm. Analysis Elemental: Found: C, 84.83 ; N, 4.31; H, 5.13. C<sub>91</sub>H<sub>66</sub>MgN<sub>4</sub>O<sub>3</sub>: requires C, 84.87; N, 4.35; H, 5.17%.

**MnCl-Porph-O-Py<sub>2</sub>G<sub>1</sub> (4d):** Porph-O-Py<sub>2</sub>G<sub>1</sub> (50 mg, 0.039 mmol) and MnCl<sub>2</sub>·4H<sub>2</sub>O (59 mg, 0.29 mmol) following the metallation method B. The metallated porphyrin product was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/Hexane 9:1 then CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9.5/0.5). Compound **4d** was obtained as a green solid (43 mg, 81%). MS (MALDI-TOF) m/z calculated for C<sub>91</sub>H<sub>66</sub>MnN<sub>4</sub>O<sub>3</sub>Cl [M-Cl]<sup>+</sup>: 1318.49; Found 1,320.62. UV-Vis:  $\lambda$ max (THF) / nm 344, 369, 396, 474 ( $\varepsilon$  / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 123 000, 59 000, 52 500, 119 000), 580 and 623 nm. Analysis Elemental: Found: C, 80.75; N, 4.13; H, 4.88. C<sub>91</sub>H<sub>66</sub>MnN<sub>4</sub>O<sub>3</sub>Cl: requires C, 80.73; N, 4.14; H, 4.91%.

#### 3. Results and Discussion

#### 3.1. Synthesis and Characterization

Compounds **1** and **2** were synthesized according to the method previously published by us<sup>60,61</sup> and following the synthetic route reported by Lindsey<sup>62</sup>. A mixture of pyrrole, benzaldehyde and 4-hydroxybenzaldehyde in anhydrous dichloromethane was reacted in the presence of borontrifluoride dietherate and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to obtain the corresponding porphyrinic units (**Scheme 1**).

The synthesis of compounds **3** and **4** was carried out by a convergent synthesis, using compound **2** as the porphyrinic core and the corresponding pyrene labeled dendron of zero and first generation, previously reported by us too.<sup>46,59</sup> Compound **2** and the corresponding bromide of generation zero and one were reacted by a Williamson reaction protocol, using  $K_2CO_3$  as base and acetone as solvent to produce zero generation

dendronized porphyrin **3** and using DMF as solvent to obtain the first generation dendronized porphyrin **4**.

In order to find the proper reaction conditions for the metallation of the porphyrins, reactions were performed using the free-base **TPP** and various solvents such as acetone, dichloromethane, chloroform, leading to successful metallations affording the different M-[TPP] complexes. However, the resulting dendrimers turned out to be poorly soluble in the above-mentioned solvents, leading to choose DMF as the best solvent for their synthesis.

Metalloporphyrins were synthesized using zinc acetate<sup>63,64</sup> or copper <sup>65</sup>, magnesium <sup>65</sup> and manganese chlorides <sup>66</sup>. In the case of the porphyrins including Zn, Cu and Mg, neutral M(II) complexes were obtained, whereas in the case of the Mn-porphyrins derivatives the metal ion was found in a Mn(III) oxidation state, this being inferred from the UV-Vis spectra/data previously reported.<sup>67,68</sup> In good agreement with Mn(II) being reported to be unstable and easily oxidized to Mn(III).

For each of the reactions, the free base porphyrins were dissolved in DMF until the solutions became homogeneous and then the corresponding metallic salt was added. The reaction mixture was sonicated in order to properly dissolve all components and heated according to the conditions reported in the experimental section. These reactions were carried out under an inert atmosphere and monitored by UV-Vis spectroscopy.



Scheme 1. General scheme of synthesis. Reaction conditions: I. (1)  $CH_2Cl_2$ , Pyrrole, rt, 15 min (2)  $BF_3$ -OEt<sub>2</sub>, rt, 15 min (3) DDQ, rt, 1h. 1) 17%, 2) 14% II. DMF, M-[L], heating. III. Acetone,  $Py_1G_0Br$ ,  $K_2CO_3$ , 18-C-6, reflux, 72h, 96%. IV. DMF,  $Py_2G_1Br$ ,  $K_2CO_3$ , 18-C-6, reflux, 72h, 96%.

The <sup>1</sup>H NMR spectrum of Porph-O-PvG<sub>0</sub> (Figure 1) shows a signal at 8.91-88.85 ppm due to protons H7, H8, H12 and H13 of the porphyrin nucleus. In the region of 8.26-819 are the signals corresponding to 6 protons of the H2 phenolic ring and between 7.83 and 7.76 a signal corresponding to the porphyrinic protons (H1, H3) integrates to 9 protons. The signal corresponding to the protons H2' and H3' appears as doublets at 8.14 and 7.29 ppm respectively, integrating to two protons each. Two triplets due to the protons H5' and H8' can be observed at 4.35 and 3.59 integrating for 2 protons  $\alpha$  and 2 protons  $\delta$  of the aliphatic chain. In the same way, we observe a multiple signal between 2.31 and 2.18 ppm due to the protons H6' and H7' integrating for 4 protons. The internal NH protons of the porphyrin appear at -2.74 ppm integrating for two protons. The signals corresponding to the pyrene protons were observed in the spectrum as a doublet at 8.43 ppm integrating for one proton, a multiplet at 8.26-8.19 ppm integrating for 4 protons as well as a multiplet at 8.09-8.0 ppm integrating for 4 protons, correspond to the total of expected protons for the pyrene ring. On the other hand, the <sup>1</sup>H spectrum of Porph-O-Py<sub>2</sub>G<sub>1</sub> (Figure 2) is similar to that of the generation zero compound, with an additional singlet at 5.18 ppm corresponding to the benzylic protons H5' integrating to two protons, a doublet at 6.83 ppm due to the ortho protons of the benzyl ring H7' integrating for 2 protons, a triplet at 6.63 ppm corresponding to the proton for the benzyl ring H8' integrating for one proton, the signals of the aliphatic chain integrate for 4 protons  $\alpha$  and 4 protons  $\delta$ . Likewise an increase in the integration of protons  $\beta$  and  $\gamma$  of the same chain (8 protons) and of the pyrene protons is observed, integrating for 18 protons.









The characterization of the metallated porphyrins was performed by absorption and mass spectrometry techniques in order to confirm the formation of the desired structures. In the absorption spectra of the complexes, the reduction from 4 to 2 Q bands is a good indication that the metallation reactions occurred. Furthermore the formation of the complexes was confirmed by MALDI-TOF mass spectrometry using dithranol as a matrice. In each case the expected mass was obtained.

#### 3.2. Absorption spectra of the dendronized porphyrins

The UV-Vis absorption spectra of all the compounds were measured using THF as solvent. In the absorption spectra of the free-base porphyrins 1, 3 and 4, the characteristic Soret band as well as the Q bands of this chromophore were observed (Figure 3 A-C). The Soret band is observed at 416 nm with high molar absorption coefficients (Table 1), corresponding to the  $S_0 \rightarrow S_2$  transition. Four bands of low intensity (Q bands) were observed at 513, 548, 593 and 649 nm, which are due to the  $S_0 \rightarrow S_1$  transition. Additionally, the absorption spectra of compounds 3 and 4 show a characteristic band for the pyrene chromophore at 344 nm, arising from the  $S_0 \rightarrow S_2$  transition. An increase of the molar absorption coefficient of this band was observed according to the number of pyrene units present in the constructs (Table 1).

When comparing the absorption spectra of the free-base porphyrin with those of the metallated porphyrins, various changes can be observed, such as a shift of the Soret band as well as a reduction in the number of Q bands. Those changes are characteristic for the metallation of porphyrins and are a good indication that the metallation occurred in the

corresponding porphyrins. All the absorption wavelengths and molar absorption coefficients of the metalloporphyrins are reported in **Table 1**.

The absorption spectra of the metallated porphyrins show an intense Soret band with a hypsochromic shift for the Cu complexes (**Figure 3 G-I**) and a bathochromic shift for Zn (**Figure 3 D-F**) and Mg complexes (**Figure 3 J-L**). Two Q bands of lower intensity are observed in the case of Zn and Mg and only one Q band is observed in the case of Cu.<sup>64</sup> For the porphyrin-Mn(III) derivative the absorption spectra changed drastically (**Figure 3 M-O**), here the Soret band is divided in two with lower molar extinction coefficients, both bands appearing at 369 and 476 nm, respectively. <sup>67</sup> This can be due to a stronger interaction between the metal and the porphyrin Q bands <sup>69</sup>

As observed in the free-base porphyrin series, the absorption spectra of the pyrene labeled dendronized metalloporphyrin compounds exhibit an additional band at 344 nm corresponding to the  $S_0 \rightarrow S_2$  transition of the pyrene chromophore with an increase in its molar absorption coefficient according to the number of pyrene units in the molecular construct. In the case of the porphyrin metallated with Mn, the absorption bands of metallated porphyrin center overlap with the absorption bands of the pyrene chromophore. However, the obtained molecular coefficient corresponds to the sum of the individual components indicating that no interaction is taking place in the ground state. This observation is true for all the compounds presented in this study.



Figure 3. Normalized absorption spectra recorded in THF. A) Free base porphyrin 1. B) Free base porphyrin 3. C) Free base porphyrin 4. D) 1 and Zn-porphyrin 1a. E) 3 and Zn-porphyrin 3a. F) 4 and Zn-porphyrin 4a. G) 1 and Cu-porphyrin 1b. H) 3 and Cu-porphyrin 3b. I) 4 and Cu-porphyrin 4b. J) 1 and Mg-porphyrin 1c. K) 3 and Mg-porphyrin 3c. L) 4

and Mg-porphyrin 4c. M) 1 and Mn-porphyrin 1d. N) 3 and Mn-porphyrin 3d. O) 4 and Mn-porphyrin 4d.

Table 1.	Absorption	coefficients	of the	porphyrinic	compounds	with	their	respective	absorption
bands.									

	Pyrene and	Soret Bands	Q Bands		
Compound	λ (nm) <sup>a</sup>	$\epsilon (dm^3 mol^{-1} cm^{-1})$	λ (nm) <sup>c</sup>		
1	416	451 000	513, 548, 593,649		
<b>1a</b> <sup>63,64</sup>	423	661 500	556, 593		
<b>1b</b> <sup>65</sup>	415	439 500	540 <sup>64</sup>		
1c <sup>65</sup>	429	552 500	571, 613		
1d <sup>66</sup>	344	23 400			
	36967	35 000	586 623		
	39667	31 500	580, 025		
	476 <sup>67</sup>	69 000			
3	344	63 000	513 548 503 640		
5	417	467 000	515, 548, 595, 049		
30	344	55 000	556 503		
Ja	424	579 000	550, 595		
3b	344	50 000	540		
	416	495 000	540		
3c	344	48 000	571 613		
	430	453 000	571,015		
	344	79 000			
3d	369	50 000	580 623		
54	396	50 500	500, 025		
	474	96 500			
4	344	101 000	512 549 592 648		
-	418	456 000	512, 549, 592, 646		
49	344	99 000	556 593		
та	424	614 500	550, 575		
4h	344	83 000	540		
10	416	434 500			
4c	344	83 500	571 613		
	430	506 000			
	344	123 000			
4d	369	59 000	580, 623.		
	396	52 500			

476	119 000		
1 = 6	110.000	1	

<sup>a</sup>Maximum absorption wavelength of the pyrene unit and the Soret band for each compound. <sup>b</sup>Values of the absorption coefficients calculated at the pyrene unit and Soret band of the porphyrin. <sup>c</sup> Absorption wavelength for Q bands.

#### 3.3 Emission Spectra of the dendronized porphyrins

The fluorescence emission spectra of the free-base and metallated porphyrins were measured in THF at room temperature by taking the necessary precautions as previously reported by our research group.<sup>46</sup> Excitations were performed at 344 nm for the pyrene band as well as at the wavelength corresponding to the Soret band of each compound. All measurements were made with the same absorbance of approximately 0.05 at the excitation wavelength.

The obtained fluorescence spectra are shown in **Figures 4** when the excitation was performed at the Soret band and in **Figure 5** when excited at the wavelength of the pyrene band (344 nm). In all spectra, the emission is reported as absolute fluorescence intensity, which means that the total integration of the emission spectra corresponds to the calculated quantum yield listed in **Table 2**.

When the Soret band is excited, the transitions  $S_{(1,0)} \rightarrow S_{(0,0)}$  for the free base porphyrins are observed approximately at 652 nm and for the porphyrin derivatives including Zn, Mg and Cu at 600, 630 and 650 nm respectively. The transitions of lower energy  $S_{(1,0)} \rightarrow S_{(0,1)}$  for the non-metallated porphyrins are observed at approximately 717 nm and for those metallated with Zn, Mg and Cu at 655, 680 and 714 respectively (**Figures S9-S12**, Supporting Information).

A comparison of the quantum yields of the series of compounds studied when excited at the wavelength of the Soret band, higher values were observed for the complexes

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with magnesium followed by those of zinc. The complexes of copper and manganese exhibited very weak or no fluorescence at all. Increasing the generation of the dendrimer leads to a slight decrease in the quantum yields of all the metallated porphyrin series.

Furthermore, when the compounds were excited at the pyrene band (344nm), residual emission from pyrene at 376 nm as well as emission from the porphyrinic moiety were observed. The calculated quantum yields between 0.002 and 0.026 for the emission of pyrene revealed a drastic quenching compared with the quantum yield of 1-pyrenbutanol (Py-But-OH,  $\varphi$ =0.524) (**Table 2**). This indicates that a very efficient energy transfer form pyrene to the metallated porphyrins is taking place in all cases. The quantum yield of the porphyrinic moiety when excited at 344 nm is lower than when excited directly at the corresponding Soret band. However, as observed for the direct excitation of the porphyrin moiety, the complexes of Mg exhibit higher quantum yields. The same trend is observed for the emission of the metalloporphyrin series through direct excitation , following this order: Mg > Zn > Cu >> Mn (Figure 5).



Figure 4. Emission spectra recorded in THF: A) Free base porphyrin 1 and metalation series 1a, 1b, 1c, 1d excited at the Soret band (see Table 1). B) Free base porphyrins 3 and metalation series 3a, 3b, 3c, 3d excited at the Soret band (see Table 1). C) Free base porphyrins 4 and metalation series 4a, 4b, 4c, 4d excited at the Soret band (see Table 1).



**Figure 5.** Emission spectra in THF of free base and metallated porphyrins series excited at 344 nm. The sharp peak at 688 nm corresponds to the harmonic (double the excitation wavelength).

Compound	λ <sub>Em-ma</sub>	<sub>x</sub> (nm) <sup>a</sup>	φ (Pyrene) λ <sub>Ex</sub> =344 <sup>b</sup>	φ (Porph) λ <sub>Ex</sub> =344 °	φ (Porph) λ <sub>Ex</sub> =Soret Band <sup>d</sup>	E <sub>Fret</sub> e	
2	-	652	-	-	0.094	-	
Py-But-OH	376	-	0.524	-	-	-	
1	-	650	-	-	0.110	-	
1a	-	600	-	-	0.064	-	
1b	-	652	-	-	0.015	-	
1c	-	617	-	-	0.217	-	
1d	-	nd	-	-	nd	-	
3	375	652	0.021	0.010	0.110	0.96	
<b>3</b> a	375	603	0.026	0.004	0.061	0.95	
3b	375	652	0.007	0.001	0.002	0.99	
3c	376	618	0.009	0.012	0.194	0.98	
3d	375	nd	0.006	nd	nd	0.98	
4	376	652	0.002	0.005	0.060	0.99	
<b>4a</b>	376	602	0.005	0.004	0.053	0.99	
4b	376	nd	0.002	0.0002	nd	0.99	
4c	376	618	0.009	0.011	0.185	0.98	
4d	376	nd	0.005	nd	nd	0.99	

 Table 2. Quantum yields and FRET efficiencies of porphyrin compounds.

<sup>a</sup> Excitation wavelength for the pyrene and the Soret bands for each compound. <sup>b</sup> Quantum yields were determined using quinine in 1 M H<sub>2</sub>SO<sub>4</sub> solution as standard ( $\varphi$ =0.54)<sup>70,71</sup>. <sup>c</sup> Quantum yield of the porphyrin core that has suffered FRET from an excited pyrene to the porphyrin, using TPP in a THF solution as standard ( $\varphi$ =0.11). <sup>d</sup> Quantum yields were determined using TPP in THF solution as standard ( $\varphi$ =0.11). <sup>e</sup> FRET efficiencies were calculated with the subsequent equation: E<sub>FRET</sub>=1–I(Py+Porphyrin)/I(Py), where I(Py+Porphyrin) is the integration of the residual emission of pyrene when linked to the porphyrin acceptor and I(Py) is the integration of the emission of pyrene in the absence of the porphyrin acceptor. **nd:** Indicates that the compound is not presenting emission at the specified wavelength.

The Förster radius for pyrene-porphyrin donor-acceptor pair was calculated using

equation 1 in order to ensure that FRET can take place in the constructs.

$$R_0 = 9790(k^2 n^2 \phi_D J(\lambda))^{\frac{1}{6}}$$
 (Eq.1)

Where  $R_0$  is the Förster radius, k is the orientation factor, n is the refractive index of the solvent,  $\varphi_D$  is the quantum yield of the donor and J( $\lambda$ ) is the overlap integral of the pyrene/porphyrin pair of chromophores. The spectral overlap was calculated using **equation 2**:

$$J(\lambda) = \frac{\int_{0}^{\infty} F_{D}(\lambda) \varepsilon_{A}(\lambda) \lambda^{4} d\lambda}{\int_{0}^{\infty} F_{D}(\lambda) d\lambda}$$
(Eq. 2)

where  $F_D(\lambda)$  is the fluorescence of the normalized emission spectra of the donor at  $\lambda$ ,  $\epsilon_A(\lambda)$  is the extinction coefficient of the acceptor at  $\lambda$ .<sup>70</sup>

In order to calculate the Förster radius in the constructs of the series of compound **3**-**3d** and **4-4d**, the optical properties of the separate donor and acceptor groups were taken into account. The superposition integral for the specific donor-acceptor pair was calculated starting from the absorption spectra of the 1a, 1b, 1c, 1d acceptor series and the emission spectrum of 1-pyrenbutanol (Py-But-OH) as donor. Compounds with the highest Förster radius were 1 and Cu complex 1b with values of 4.8 nm each. In the case of the Zn 1a and Mg 1c complexes, the Förster radius was very similar, giving calculated values of 4.6 and 4.5 nm, respectively. The lowest spectral overlap was observed for the Mn complex 1d, where the Förster radius resulted to be the smallest of this series with a value of 3.9 nm. In a previous report from our group, the distance between donor and acceptor in a similar type of compound was calculated in its extended conformation. A distance of 3 nm was calculated for first generation dendrimers. <sup>46</sup> The constructs in solution will not be found in this conformation but rather in a coiled conformation, allowing both chromophores to get even closer to each other. Since the distance between the chromophores is smaller than the estimated Förster radius, it can be concluded that in all cases an efficient energy transfer is taking place between the pyrene and the metallated phorphyrin acceptor.

By exciting the dendronized porphyrin compounds at 344 nm, energy transfer from the pyrene containing dendrones to the metallated porphyrin core can be observed. The

fluorescence intensity of the acceptor ([M]-Porphyrin) is observed at naked eye, since the emission wavelength in the red part of the spectrum is very different than the one from the pyrene donor, indicating that the FRET is taking place from the pyrene group. The obtained values for the FRET efficiencies are reported in **Table 2**. In all cases, those values are almost equal to one, suggesting the efficient energy transfer in the metallated pyrene dendronized porphyrin.

#### 3.4 Time-Resolved Fluorescence Measurements

Time-resolved fluorescence measurements for all the compounds were performed in THF by Time Correlated Single Photon Counting (TCSPC) experiments. Decay profiles were measured by excitation at 344 nm for the pyrene moiety and at 425 nm for the porphyrin moieties and recorded at the wavelengths corresponding to the emission of the pyrene donor and the metalloporphyrin acceptor, respectively. The lifetime data of all the compounds of this study are reported in **Tables 3** to **5**. The data were fitted using Decay Analysis Software (DAS6) from Horiba Scientific and Instrument Response Function (IRF). Values between 1 and 1.5 were obtained for  $\chi^2$  and the plots of the residuals showed a random distribution corroborating that good fits were obtained in all cases.

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Compound	a <sub>1</sub>	τ <sub>1</sub> (ns)	a <sub>2</sub>	$\tau_2$ (ns)	<b>a</b> <sub>3</sub>	τ <sub>3</sub> (ns)	<b>a</b> 4	τ <sub>4</sub> (ns)	<t><t><t>(ns)</t></t></t>	χ <sup>2</sup>
3	32.952	0.06	0.036	3.90	0.037	20.57	0.011	77.39	0.1	1.23
<b>3</b> a	2.050	0.16	0.012	7.38	0.060	77.60	-	-	2.4	1.09
3b	1.317	0.21	0.028	9.26	0.021	35.52	0.020	193.77	3.7	1.2
3c	2.240	0.18	0.016	2.61	0.005	15.31	0.004	112.62	0.4	1.08
3d	2.259	0.17	0.022	7.11	0.013	33.56	0.012	189.24	1.4	1.21
4	0.327	0.80	0.031	5.56	0.010	28.22	0.003	164.39	3.1	1.39
4a	1.309	0.25	0.015	4.84	0.005	24.65	0.002	179.08	0.7	1.14
4b	0.405	0.34	0.007	2.57	0.002	14.35	0.0004	125.11	0.6	1.33
4c	0.880	0.35	0.011	5.43	0.008	25.09	0.003	116.84	1.0	1.13
4d	0.864	0.35	0.011	6.07	0.008	26.63	0.003	124.76	1.0	1.17

**Table 3**: Pre-exponential factors and decay times for the pyrene momomer recorded at 378 nm in THF for all the constructs.

Compound	<7> (ns)	χ²	Compound	<7> (ns)	$\chi^2$
3	11.6	1.29	4	12.2	1.26
<b>3</b> a	1.8	1.59	4a	1.8	1.92
3b	nd	nd	4b	nd	nd
3c	6.4	1.24	4c	6.4	1.33
3d	nd	nd	4d	nd	nd

**Table 4**: Decay times for the porphyrin moiety recorded at  $\lambda_{ex} = 344$  nm and  $\lambda_{em} =$  maximum of the porphyrin emission<sup>a</sup> in THF for all the constructs after the FRET process has occur.

<sup>a</sup> See **Table 2**. nd Indicates that the compound is not presenting emission at the specified wavelength.

**Table 5**: Decay times for the porphyrin moieties recorded at  $\lambda_{ex}$  = Soret Band<sup>a</sup> and  $\lambda_{em}$  = maximum of the porphyrin emission<sup>b</sup> in THF for all the constructs.

Compound	(ns)	χ²	Compound	<7> (ns)	χ²	Compound	<τ> (ns)	χ²
1	12.5	1.14	3	11.9	1.18	4	12.0	1.16
1a	2.0	1.39	<b>3</b> a	1.7	1.25	4a	1.8	1.42
1b	10.3°	1.30	3b	10.4°	1.38	4b	nd	nd
1c	7.0	1.16	3c	6.3	1.18	4c	6.3	1.3
1d	nd	nd	3d	nd	nd	4d	nd	nd

<sup>a</sup> See **Table 1**. <sup>b</sup> See **Table 2**. <sup>c</sup> Decays of the porphyrin metallated with Cu were found to be biexponential; **1b**  $a_1 = 0.007$ ;  $\tau_1 = 2.2$ ;  $a_2 = 0.041 \tau_2 = 11.7$ ; **3b**  $a_1 = 0.010$ ;  $\tau_1 = 3.1$ ;  $a_2 = 0.044 \tau_2 = 12.0$ . nd Indicates that the compound is not presenting emission at the specified wavelength. Donor and acceptor fluorescence decay kinetics were measured in order to study the energy transfer in all the constructs. As previously reported by our group, the formation of excimers in the compounds bearing two pyrene moieties is excluded due to the fact that the rate constant of excimer formation is much lower than the rate constant of energy transfer.<sup>47</sup> Emission spectra presented in **Figure 5** showed almost no emission of the pyrene excimer for the **4-4d** series even though two pyrene units are present in this series. Therefore residual excimer emission would be due to free dendrons and can be omitted.

The obtained decay profiles following excitation at 344 nm and recorded at 378 nm, which corresponds to the emission of the monomer of the pyrene unit, were fitted using 4 exponentials parameters (**Table 3**). Decay profiles from the porphyrin or metalloporphyrin moieties following excitation at the pyrene moiety (344 nm) were fitted with mono exponential parameters except for the porphyrin metallated with Cu, which decays were fitted using biexponential parameters (**Table 4**). The obtained lifetime at the porphyrin emission wavelength corresponded to the lifetime of the respective TPP and metallated TPP excited at the Soret bands (**Table 5**).

The initial fluorescence lifetime of the donor corresponds to the lifetime of the precursor 1pyrenebutanol in THF, which was determined to be 190 ns. The lifetimes of the porphyrin and metalloporphyrin acceptors were obtained by fitting the fluorescence decay of the series **1-1d** recorded at their respective emission maximum (**Table 5**). The decays of the porphyrin emission are largely affected by the coordinated metallic ion, the fastest decay was observed for Zn ( $\tau = 1.8$  ns) followed by Mg ( $\tau = 6.4$  ns) and Cu ( $\tau = 10.4$  ns), while Mn caused the total quenching of the emission of the porphyrin moiety.

In the molecular constructs where the donor and the acceptor are linked (series **3-3d** and **4-4d**), the excited state lifetime of the pyrene donor moiety is decreased. The decay of the pyrene monomer

recorded at 378 nm is indistinguishable from the instrument response function in the early time, which is an indication of an efficient and fast FRET process. In **Figure 6**, the fluorescence decays of compound 3c and 4c are presented. They are representative for the decays of the other compounds of this study. All the decays with residual plots can be found in the Supporting Information. In Figure 6, the difference in decay time between the donor, acceptor and donoracceptor construct can be appreciated. At the early time of the fluorescence decay of compound 3c and 4c a very short decay time is a good indication for a fast FRET process. The average rate constant for FRET was calculated and was found to be in the same order of magnitude than previously reported in our group.<sup>47</sup> The emission that produces the long time decay is due to unquenched pyrene moieties. Small amount of pyrene impurities or less than 100% efficiencies for the FRET process are responsible for the detection of long lifetime decay. FRET efficiencies calculated based on time-resolved fluorescence measurements are corresponding to FRET efficiencies obtained by steady state fluorescence measurements and are found to be almost quantitative with values higher than 98 % for all the compounds studied (Table 6). Metallation of the porphyrin moiety was not affecting the FRET process from pyrene to porphyrin. In all cases, the decay of the pyrene monomer showed efficient FRET process.



**Figure 6**: Time-resolved emission data for compounds **3c** (A) and **4c** (B) in THF. ( $\lambda_{ex} = 344$  nm;  $\lambda_{em} = 378$  nm) Decays of 1-pyrenebutanol donor ( $\lambda_{ex} = 344$  nm;  $\lambda_{em} = 378$  nm) and acceptor compound **1c** ( $\lambda_{ex} = 425$  nm;  $\lambda_{em} = 617$  nm) were added to both plots as comparison.

Compound	$< k_{FRET} > s^{-1}$	E <sub>FRET</sub>	Compound	<k <sub>FRET</sub> $>$ s <sup>-1</sup>	E <sub>FRET</sub>
3	91 × 10 <sup>9</sup>	0.99	4	0.3 × 10 <sup>9</sup>	0.98
<b>3</b> a	$4.2 \times 10^{9}$	0.98	4a	$1.4 \times 10^{9}$	0.99
3b	$2.7  imes 10^9$	0.98	4b	1.8 × 10 <sup>9</sup>	0.99
3c	$23 \times 10^9$	0.99	4c	$1.0 \times 10^{9}$	0.99
3d	$7.2 \times 10^{9}$	0.99	4d	$1.0 \times 10^{9}$	0.99

**Table 6**: Average rate constant for FRET ( $\langle k_{FRET} \rangle s^{-1}$ )<sup>a</sup> and FRET ( $E_{FRET}$ )<sup>b</sup> efficiencies for compounds series **3-3d** and **4-4d**.

<sup>a</sup><k<sub>FRET</sub>> was calculated using the following equation: <k<sub>FRET</sub>> = (1/< $\tau$ >)-(1/ $\tau$ <sub>D</sub>) where < $\tau$ > is the average lifetime of the pyrene monomer given in **Table 3** and  $\tau$ <sub>D</sub> is the lifetime of the pyrene monomer donor which is equal to 190 ns. <sup>b</sup>E<sub>FRET</sub> was calculated using following equation: E<sub>FRET</sub>=1-(< $\tau$ >/ $\tau$ <sub>D</sub>), where < $\tau$ > is the average lifetime of the pyrene monomer given in **Table 3** and  $\tau$ <sub>D</sub> is the lifetime of the pyrene monomer donor which is equal to 190 ns.

#### 4. Conclusions

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A novel series of dendronized porphyrins of generations zero and one bearing one and two pyrene groups in the periphery were synthesized and successfully characterized. The metallation of these dendronized compounds with Zn, Cu, Mg and Mn was successfully performed. The absorption spectra of the metallated dendronized porphyrins with pyrene groups exhibited the characteristic bands of the non-metallated porphyrins, with a shift in the Soret band and a decrease in the number of Q bands, confirming that the metallation took place. Regarding the emission of the obtained metallated dendronized porphyrins, the higher quantum yields were obtained for the Mg derivative followed by Zn compound. In the case of Cu and Mn complexes, very weak or no emission was detected. When excited at the absorption band of pyrene, only weak residual absorption of this chromophore was observed and the corresponding emission bands of the metallated porphyrins appeared. This observation as well as the calculated Förster radius indicate that FRET takes place in metallated dendronized porphyrins with donor-acceptor groups (pyrene-metallated porphyrin) with values above 95% in all these systems, being a highly efficient energy transfer phenomenon.

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Energy transfer studies were performed on a series of new pyrene-metalloporphyrin (Zn, Cu, Mg and Mn) dendritic constructs.