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COMMUNICATION

Synthesis and Photophysical Properties of a Series of Novel Porphyrin Dendrimers Containing Organoiron Complexes

Mosa Alsehli[1,2] · Shaya Y. Al-Raqa[1] · Inan Kucukkaya[2,3] · Paul R. Shipley[2] · Brian D. Wagner[3] · Alaa S. Abd-El-Aziz[2,3]

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Abstract

This article is focused on the design and photophysical properties of a series of novel porphyrin and metalloporphyrin dendrimers containing cationic η^6-chloroarene-η^5-cyclopentadienyliron(II) complexes functionalized with naphthalene and capped with ferrocene. The incorporation of cationic η^6-chloroarene-η^5-cyclopentadienyliron moieties into the dendrimer structures enhances solubility, and facilitates nucleophilic aromatic substitution and addition reactions due to the intense electron-withdrawing ability of the iron center. Divergent approaches were employed to yield highly symmetrical branched materials, with interesting and potentially useful properties. The preparation of these dendrimers was achieved via metal-mediated nucleophilic aromatic substitutions and Steglich esterifications. These dendrimers and their precursors were characterized through nuclear magnetic resonance spectroscopy, infrared spectroscopy, and UV–Visible and fluorescence spectroscopy. Substitution on the porphyrin core with various side chains and terminal functional groups and chromophores had little impact on the porphyrin emission properties, allowing for a wide variety of fluorescent macromolecules to be prepared which retain this characteristic emission. Also, the presence or absence of the organopyrene moieties also had little effect on the emission from these compounds. Complexation of a metal cation, such as Zn^{2+}, by these compounds, did however result in a significant blue shift in the observed fluorescence; this interesting result has the potential for applications in the development of fluorescent-based cation sensors.

Keywords Organoiron · Dendrimers · Porphyrins

1 Introduction

The study of dendrimers has received significant interest in recent years [1–5]. Dendrimers are highly symmetric and possess well-defined nanostructures. Their synthesis involves a much larger degree of control than does that of linear polymers, and as a result, dendrimers are much more monodisperse and thus have useful and controllable materials properties. As a result of their unique physical and chemical properties, dendrimers have been the focus of many recent studies and applications [4], including those involving electron-transfer processes [5].

Porphyrins and metalloporphyrins display interesting and unique photophysical, photochemical and electrochemical properties. They play essential roles in biological activities such as photosynthesis. They have useful applications in many fields such as light-energy conversion [6–8], photodynamic therapy [9, 10] and other areas of photomedicine [11], third-order nonlinear optical materials [12–14], fluorescence switches [15] and molecular wire [16–19]. Interestingly, unique porphyrin-based supramolecular architectures have also been prepared through self-assembly [20]. Most interestingly, porphyrins have been used as the core for the preparation of dendrimers; such materials are the focus of this paper.

The first synthesis of dendrimer-based on a porphyrin core was reported in 1993 by Aida and co-workers. In their

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✉ Alaa S. Abd-El-Aziz
abdelaziz@upei.ca

[1] Department of Chemistry, Taibah University, P.O. Box 344, Madinah, Saudi Arabia

[2] Department of Chemistry, University of British Columbia Okanagan, 3333 University Way, Kelowna, BC V1V 1V7, Canada

[3] Department of Chemistry, University of Prince Edward Island, Charlottetown, PEI C1A 4P3, Canada

approach, a porphyrin unit was integrated into the center of poly (benzyl ether) dendrimer to form a synthetic model of a hemoprotein [21]. A year later Diederich and co-workers reported on the synthesis and redox properties of a porphyrin-based poly (ether-amide) dendrimer [22]. Two years later Suslick and co-workers prepared a series of manganese porphyrin-core poly (aryl ester) dendrimers, and tested them for their oxidation properties [23]. Since that early work on dendrimers based on porphyrin cores, other interesting examples with unique properties and features have been reported, including in the past few years [24–26], demonstrating the utility of the porphyrin-core dendrimer motif.

Dendrimers containing ferrocene (redox-active moieties) and porphyrin or metalloporphyrin units in their molecular structure are of great interest as hosts for anion recognition [27, 28]. The facile synthesis of such dendrimers containing diverse multifunctional groups is substantially attributed to the high control in the synthesis of these hyperbranched porphyrin cores. Most of the dendrimers with porphyrin cores have been synthesized by the introduction of dendritic substituents at the meso-positions of the porphyrin by either a convergent or a divergent approach [29]. In this paper, we demonstrate the utility of incorporating cationic cyclopentadienyliron moieties into such porphyrin-core dendrimers, as the strong electron withdrawing ability of the iron in these moieties, results in easy facilitation of the nucleophilic aromatic substitution and addition reactions [30, 31].

During the past two decades, our group has reported the synthesis of numerous examples of iron-containing macromolecules, including hyperbranched polymers with ether and ester linkages and azo dye-containing dendritic species based on upper rim functionalized organoiron metallocalix [4] arenes [32–35]. Furthermore, our group has reported the preparation of star-shaped oligomers containing cationic cyclopentadienyliron complex with azo chromophores [36]. In this paper, we bring together all of these unique aspects discussed above, by reporting the first examples of dendrimers containing in a single molecule cyclopentadienyliron, ferrocene and porphyrin units. These new types of interesting and applicable macromolecules have been fully characterized, and show interesting spectroscopic and particularly emissive properties, with potentially useful applications as cationic optical sensors, as will be discussed.

2 Experimental

2.1 Materials

The synthesis of compounds **8, 9**, and **13** was achieved using a previously published methodology [30, 31]. Pyrrole was redistilled before used. All of the others reagents were purchased from Sigma-Aldrich and used without further purification. All reactions and complexes containing an η^6-dichlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate moiety were kept in the dark to prevent photochemical decomposition.

2.2 Characterizations

^{1}H and ^{13}C NMR spectra were recorded at 400 and 101 MHz, respectively on a Varian Mercury Plus spectrometer equipped with a gradient field probe, with chemical shifts referenced to residual solvent peaks and coupling constants reported in Hz. A Varian Cary 100 Bio UV–Visible spectrophotometer was used to conduct UV–Visible absorption measurements and a Horiba Scientific QuantaMaster 400 Steady State Spectrometer was used to measure all fluorescence spectra, in both cases a standard 1 cm^2 quartz fluorescence cell was used.

2.3 Synthesis of 5,10,15,20-Tetrakis(4-Hydroxyphenyl) Porphyrin 1a (T(P-OH)PPH$_2$)

p-Hydroxylbenzaldehyde (40 mmol) was dissolved in 250 mL propionic acid, stirred vigorously, and heated to reflux. To this solution, 30 mL of nitrobenzene was added. Freshly distilled pyrrole (40 mmol) in 10 mL of propionic acid was slowly added drop wise, and the reaction mixture was heated to reflux for 30 min. The reaction mixture was left to cool and stirred overnight. The mixture was filtered and the solid product was washed repeatedly with a mixture of ethanol and propionic acid (1:1 v/v), then with hot water until the rinsing solution was no longer dark. The product was air dried and then dried at 100 °C to afford the purple crystalline product. All the Detailed information on the synthesis and the characterization is provided as Supporting Information (SI).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, OH), 8.87 (s, 8H), 8.00 (d, $J = 8.5$ Hz, 8H), 7.21 (d, $J = 8.5$ Hz, 8H), −2.87 (s, N–H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.65, 135.66, 132.38, 131.95, 120.44, 114.08.

2.4 Synthesis of T(P-OH)PPNi 1b and T(P-OH)PPZn 1c

T(P-OH)PPH$_2$ (0.1 mmol) was dissolved in 30 mL methanol and 10 mL CHCl$_3$ containing nickel(II) chloride or zinc(II) chloride (0.11 mmol). The reaction mixture was heated to reflux for 4 h at 70 °C, and then cooled to room temperature. Distilled water (60 mL) was added to the mixture, chloroform and methanol were evaporated under reduced pressure. The product was filtered to give either brownish-red crystals (**1b**) or purple crystals (**1c**).

1b: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (br s, OH), 8.75 (s, 7H), 7.79 (d, $J = 8.5$ Hz, 8H), 7.13 (d, $J = 8.5$ Hz, 8H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.0, 153.5, 145.2, 142.5, 142.4, 129.6, 124.5.

1c: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (br s, OH), 8.80 (s, 8H), 7.95 (d, $J = 8.5$ Hz, 8H), 7.17 (d, $J = 8.5$ Hz, 8H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 166.5, 151.2, 144.2, 14.4, 141.3, 129.2, 124.4.

2.5 Synthesis of 2a–c

Compound **1a, 1b**, or **1c** (0.1 mmol) was reacted with η^6-chlorobenzene-η^5-cyclopentadienyliron complex **9** (0.45 mmol) and K_2CO_3 (1.5 mmol) in 20 mL DMF at room temperature under N_2 in the dark for 72 h. The reaction mixture was precipitated into 250 mL 1.2 M HCl containing NH_4PF_6. The precipitate was filtered, washed with water, and dried under reduced pressure. The product was further purified through a neutral alumina column eluting with DCM, then ethyl acetate. Yield: 82%.

2a: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06 (s, 8H), 8.41 (d, $J = 7.8$ Hz, 8H), 7.80 (d, $J = 7.8$ Hz, 8H), 6.70 (d, $J = 6.2$ Hz, 8H), 6.45 (d, $J = 6.2$ Hz, 8H), 5.46 (s, 20H), 2.48 (s, under DMSO peak), − 2.98 (br s, NH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.6, 138.7, 136.3, 131.4, 135.1 (br), 119.1, 119.0, 100.6, 86.9, 78.9, 77.6, 76.8, 19.4.

2b: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.98 (s, 8H), 8.22 (d, $J = 7.8$ Hz, 8H), 7.74 (d, $J = 7.8$ Hz, 8H), 6.69 (d, $J = 6.2$ Hz, 8H), 6.44 (d, $J = 6.2$ Hz, 8H), 5.46 (s, 20H), 2.48 (s, under DMSO peak). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.4, 142.6, 138.7, 136.3, 131.4, 135.1, 133.4, 119.1, 119.0, 100.6, 86.9, 78.9, 77.6, 76.8, 19.4.

2c: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.00 (s, 8H), 8.26 (d, $J = 7.8$ Hz, 8H), 7.76 (d, $J = 7.8$ Hz, 8H), 6.69 (d, $J = 6.2$ Hz, 8H), 6.45 (d, $J = 6.2$ Hz, 8H), 5.46 (s, 20H), 2.48 (s, under DMSO peak).

2.6 Synthesis of 3a–c

Compound **1a, 1b**, or **1c** (0.3 mmol) was reacted with η^6-dichlorobenzene-η^5-cyclopentadienyliron complex **8** (1.40 mmol) and K_2CO_3 (3.5 mmol) in 45 mL DMF at room temperature under N_2 in the dark for 72 h. The reaction mixture was precipitated into 300 mL 1.2 M HCl containing NH_4PF_6. The precipitate was filtered, washed with water, and dried under reduced pressure. The product was further purified through a neutral alumina column eluting with DCM, then ethyl acetate. Yield: 78%.

3a: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06 (s, 8H), 8.41 (d, $J = 8.2$ Hz, 8H), 7.82 (d, $J = 8.2$ Hz, 8H), 7.00 (d, $J = 6.6$ Hz, 8H), 6.86 (d, $J = 6.6$ Hz, 8H), 5.46 (s, 20H), − 2.84 (br s, NH).

3b: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.94 (s, 8H), 8.20 (d, $J = 8.4$ Hz, 8H), 7.75 (d, $J = 8.4$ Hz, 8H), 6.96 (d, $J = 6.8$ Hz, 8H), 6.80 (d, $J = 6.8$ Hz, 8H), 5.43 (s, 20H).

3c: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.95 (s, 8H), 8.21 (d, $J = 8.6$ Hz, 8H), 7.75 (d, $J = 8.6$ Hz, 8H), 6.97 (d, $J = 6.9$ Hz, 8H), 6.81 (d, $J = 6.9$ Hz, 8H), 5.44 (s, 20H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.3, 142.3, 137.8, 135.6, 132.9, 132.0, 119.4, 118.1, 103.9, 87.0, 79.5, 76.9.

2.7 Synthesis of 5a–c

Compound **3a, 3b**, or **3c** (0.2 mmol) was reacted with **11** (0.88 mmol) and K_2CO_3 (2.5 mmol) in 45 mL DMF at room temperature, under N_2, in the dark for 72 h. The reaction mixture was precipitate into 10% HCl (300 mL) containing NH_4PF_6. The precipitate was filtered, washed with water, and dried under reduced pressure. The product was further purified through a neutral alumina column eluting with DCM containing 1–3% methanol. Yield 72%.

5a: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 8H), 8.39 (d, $J = 8.3$ Hz, 8H), 8.19 (d, $J = 8.9$ Hz, 4H), 8.07 (d, $J = 7.9$ Hz, 4H), 8.03 (d, $J = 7.7$ Hz, 4H), 7.95 (d, $J = 2.1$ Hz, 4H), 7.79 (d, $J = 8.3$ Hz, 8H), 7.61 (m, 12H), 6.72 (d, $J = 6.8$ Hz, 8H), 6.54 (d, $J = 6.8$ Hz, 8H), 5.44 (s, 20H), − 2.89 (br s, NH).

5b: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (s, 8H), 8.34 (d, $J = 8.3$ Hz, 8H), 8.16 (d, $J = 8.9$ Hz, 4H), 8.04 (d, $J = 7.9$ Hz, 4H), 7.99 (d, $J = 7.7$ Hz, 4H), 7.90 (d, $J = 2.1$ Hz, 4H), 7.68 (d, $J = 8.3$ Hz, 8H), 7.60 (m, 12H), 6.72 (d, $J = 6.8$ Hz, 8H), 6.52 (d, $J = 6.8$ Hz, 8H), 5.42 (s, 20H).

5c: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (s, 8H), 8.35 (d, $J = 8.3$ Hz, 8H), 8.17 (d, $J = 8.9$ Hz, 4H), 8.05 (d, $J = 7.9$ Hz, 4H), 8.00 (d, $J = 7.7$ Hz, 4H), 7.92 (d, $J = 2.1$ Hz, 4H), 7.72 (d, $J = 8.3$ Hz, 8H), 7.60 (m, 12H), 6.72 (d, $J = 6.8$ Hz, 8H), 6.53 (d, $J = 6.8$ Hz, 8H), 5.42 (s, 20H).

2.8 Synthesis of 7a and 7c

Compound **5a** or **5c** was placed in a 50 mL Pyrex tube and dissolved with acetonitrile. The Pyrex tube was purged with N_2 and placed in a photoreactor using a xenon light source for 6 h. The resulting solution was extracted in $CHCl_3$, washed with water, and dried under $MgSO_4$. The $CHCl_3$ was removed *in vacuo* to collect the compounds.

7a: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (s, 8H), 8.23 (d, $J = 8.5$ Hz, 8H), 8.01 (d, $J = 8.9$ Hz, 4H), 7.93 (d, $J = 8.0$ Hz, 4H), 7.86 (d, $J = 8.0$ Hz, 4H), 7.55–7.41 (m, 28H), 7.38 (dd, $J = 8.9, 2.5$ Hz, 4H), 7.30 (d, $J = 9.0$ Hz, 8H).

7c: ^{1}H NMR (400 MHz, acetone-d_6) δ 8.86 (m, 8H), 8.07 (d, J = 8.2 Hz, 8H), 7.99 (m, 8H), 7.92 (d, J = 8.1 Hz, 4H), 7.83 (d, J = 8.2 Hz, 4H), 7.50 (m, 4H), 7.39–7.45 (m, 16H), 7.36 (m, 4H), 7.28 (d, J = 8.1 Hz, 8H), 7.23 (m, 4H).

2.9 Synthesis of 4a–c

Compound **3a, 3b**, or **3c** (0.3 mmol) was reacted with **10** (1.40 mmol) and K_2CO_3 (3.5 mmol) in 45 mL DMF at room temperature under N_2 in the dark for 72 h. The reaction mixture was precipitated into 300 mL 1.2 M HCl containing NH_4PF_6. The precipitate was filtered, washed with water, and dried under reduced pressure. The product was further purified through a neutral alumina column eluting with DCM, then ethyl acetate. Yield: 76%.

4a: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 8H), 8.37 (d, $J=7.0$ Hz, 8H), 7.78 (d, $J=7.0$ Hz, 8H), 7.55 (d, $J=7.6$ Hz, 8H), 7.38 (d, $J=7.6$ Hz, 8H), 6.70 (d, $J=5.9$ Hz, 8H), 6.41 (d, $J=5.9$ Hz, 8H), 5.41 (s, 20H), 4.60 (s, 8H), −2.90 (br s, NH).

4b: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.90 (s, 8H), 8.18 (d, $J=8.0$ Hz, 8H), 7.71 (d, $J=8.4$ Hz, 8H), 7.54 (d, $J=8.0$ Hz, 8H), 7.36 (d, $J=8.4$ Hz, 8H), 6.64 (d, $J=7.0$ Hz, 8H), 6.38 (d, $J=7.0$ Hz, 8H), 5.37 (s, 20H), 4.59 (d, $J=5.5$ Hz, 8H). ^{13}C NMR (101 MHz, dmso) δ = 153.93, 151.88, 142.27, 140.84, 137.42, 135.50, 132.77, 130.78, 129.83, 128.67, 120.37, 119.02, 118.08, 78.01, 75.79, 74.76, 62.18.

4c: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.95 (s, 8H), 8.21 (d, $J=8.0$ Hz, 8H), 7.74 (d, $J=8.4$ Hz, 8H), 7.54 (d, $J=8.0$ Hz, 8H), 7.37 (d, $J=8.4$ Hz, 8H), 6.66 (d, $J=7.0$ Hz, 8H), 6.40 (d, $J=7.0$ Hz, 8H), 5.39 (s, 20H), 4.59 (d, $J=5.5$ Hz, 8H).

2.10 Synthesis of 4d

Compounds **4a** was placed in a 50 mL Pyrex tube and dissolved with acetonitrile. The Pyrex tube was purged with N_2 and placed in a photoreactor for 6 h. The resulting solution was extracted in $CHCl_3$, washed with water, and dried under $MgSO_4$. The $CHCl_3$ was removed *in vacuo* to collect the compounds.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.91 (s, 8H), 8.21 (d, $J=8.16$ Hz, 8H), 7.43 (d, $J=8.81$ Hz, 16H), 7.36 (d, $J=8.81$ Hz, 8H), 7.18 (d, $J=8.54$ Hz, 8H), 7.06 (d, $J=8.54$ Hz, 8H), 4.49 (d, $J=5.5$ Hz, 8H).

2.11 Synthesis of 6a and 6c

Compound **4a** or **4c** (0.3 mmol), carboxylic ferrocene **12** (1.5 mmol), DCC (1.8 mmol), and DMAP (1.8 mmol) were stirred with 15 mL DCM and 5 mL DMF under N_2 for 24 h. The mixture was placed in a freezer to precipitate DCU. The reaction mixture was poured into 1.2 M HCl containing NH_4PF_6 and extracted into DCM. The organic layer was washed with water and dried over $MgSO_4$. The product was filtered and the solvent removed *in vacuo*. The product residue was dissolved in acetone and filtered to remove any remaining DCU. The product was precipitated into basic water to remove any excess carboxylic ferrocene. The precipitate was collected and dried under reduced pressure. Yield: 74%.

6a: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.96 (s, 8H), 8.33 (d, $J=8.1$ Hz, 8H), 7.79 (m, 16H), 7.46 (d, $J=8.3$ Hz, 8H), 6.64 (d, $J=6.6$ Hz, 8H), 6.40 (d, $J=6.6$ Hz, 8H), 5.31 (s, 20H), 4.79 (t, $J=2.0$ Hz, 8H), 4.50 (t, $J=2.0$ Hz, 4H), 4.16 (s, 20H).

6c: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (s, 8H), 8.15 (d, $J=8.1$ Hz, 8H), 7.68 (m, 16H), 7.43 (d, $J=8.3$ Hz, 8H), 6.60 (d, $J=6.6$ Hz, 8H), 6.39 (d, $J=6.6$ Hz, 8H), 5.32 (s, 20H), 4.79 (t, $J=2.0$ Hz, 8H), 4.50 (t, $J=2.0$ Hz, 4H), 4.16 (s, 20H).

2.12 Synthesis of 14a

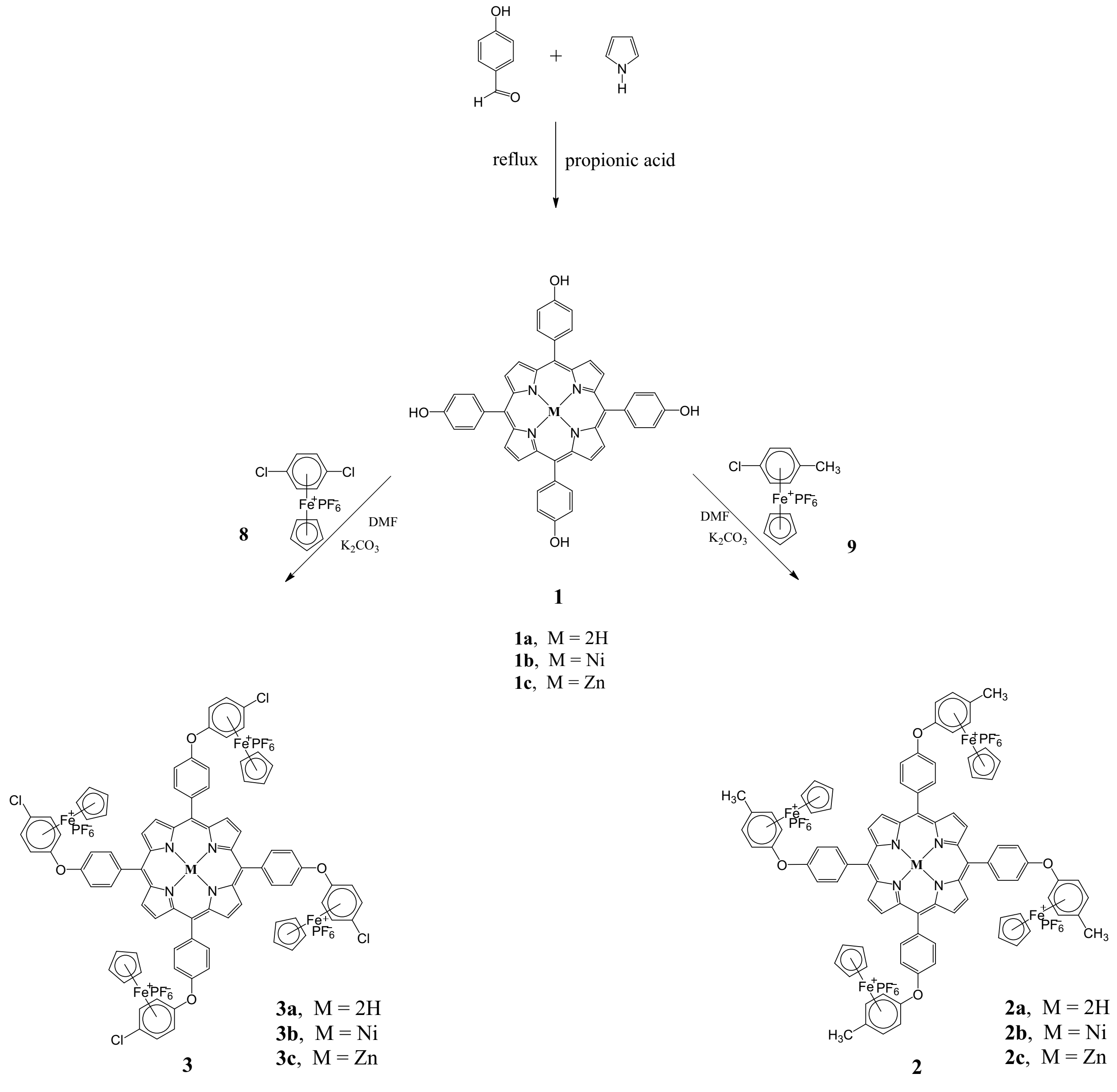
Compound **4a** (0.4 mmol), valeric bimetallic complex **13** (1.7 mmol), DCC (2.0 mmol), and DMAP (2.0 mmol) were stirred with 20 mL DCM and 10 mL DMF under N_2 for 24 h. The mixture was placed in a freezer to precipitate DCU. The reaction mixture was filtered and poured into 1.2 M HCl containing NH_4PF_6. The precipitated product was filtered and the residue was dissolved in acetone and filtered to remove any remaining DCU. The product was precipitated again into water, collected, and dried under reduced pressure. Yield: 72%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 (br s, 8H), 7.78 (br m, 8H), 7.60 (br m, 8H), 7.43, (br m, 8H), 7.40 (br m, 24H), 7.28 (br m, 16H), 6.76(br m, 16H), 6.70 (br m, 8H), 6.43 (br m, 24H), 5.28 (br s, 20H), 5.19 (br s, 40H), 5.13 (br s, 8H), 2.51 (br m, 8H), 2.27 (br m, 8H), 1.71 (br s, 12H), −2.87 (br s, NH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 26.9, 29.7, 35.9, 45.0, 64.9, 75.3, 75.9, 76.3, 77.9, 79.3, 86.8, 103.6, 118.7, 119.1, 119.9, 120.1, 120.5, 129.2, 129.3, 129.9, 130.2, 130.5, 131.9, 134.1, 136.3, 138.7, 146.0, 146.2, 151.1, 153.2.

3 Results and Discussion

η^6-Dichlorobenzene-η^5-cyclopentadienyliron complexes have been shown to readily undergo nucleophile aromatic substitution reactions under mild conditions [30, 31]. This is the motivation for the current incorporation of these types of organoiron complexes into the porphyrin-based frameworks, as this allows for a versatile method for producing functionalized porphyrins, analogous to that of other multibranched polymers and polymer stars based on other cores [32–36].

The preparation of porphyrins and metalloporphyrins based on η^6-dichlorobenzene-η^5-cyclopentadienyliron is interesting as the presence of the terminal chloro groups on the organoiron complex allows for the nucleophilic aromatic substitution reaction to continue to further functionalize the prepared porphyrin, allowing for the construction of dendrimers of varying generation. The presence of the phenolic groups on the porphyrin and metalloporphyrins rings further allows for the addition of cationic organoiron groups to the molecule. The η^6-monochlorobenzene-η^5-cyclopentadienyliron complex **9** was reacted with free-base porphyrin **1a** (5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin) or with metalloporphyrins **1b** or **1c** in DMF, with an excess amount of potassium carbonate as a base to give porphyrins **2a–c** containing four cationic organoiron moieties (Scheme 1). This reaction was carried out at room temperature, yielding deep purple colored materials. All of the detailed information on the synthesis and the characterization is provided as Supporting Information (SI). Under the same reaction conditions porphyrins **3a–c** were synthesized to produce the first step in making the target porphyrin-based dendrimers containing cationic iron moieties, ferrocene, and naphthalene (Scheme 1). The ^{1}H NMR spectrum shows that the organoiron unit was successfully attached to the porphyrin core, as evidenced by



Scheme 1 Synthesis of free-base porphyrin and metalloporphyrins 2a–c and 3a–c

the appearance of the cyclopentadienyl ring (Cp) peak at 5.46 ppm as well as all downfield shift of the phenyl and pyrrole protons (Figure S6 and S8) (SI).

The HSQC spectrum of **2a** (Fig. 1) further confirms the substitution of the iron complex onto the porphyrin core. The protons of the methyl group overlap with the DMSO solvent peak at 2.50 ppm, but nonetheless correlate well to the methyl carbon peak at 19.4 ppm. The phenyl carbons resonate at 119.1-138.7 ppm (*ortho*- and *meta*-C-Ph) and correlate to protons that resonate at 7.80–8.41 ppm respectively. The Cp protons show a correlation to a carbon which resonates at 77.6 ppm.

The presence of the cyclopentadienyliron moiety on the complexed arene allowed for the chlorine group to readily undergo further nucleophilic aromatic substitution reactions in these relatively mild conditions. The incorporation of naphthalene into a free-base porphyrin or a metalloporphyrin results in the preparation of photoactive materials with wide potential applications in different fields such as organic light-emitting diodes (OLEDs), light harvesting, or switches. Chloro-terminated free-base porphyrin **3a** and metalloporphyrin complexes **3b** and **3c** were reacted with 2-hydroxynaphthalene (**11**) in DMF in the presence of a weak base like potassium carbonate to give porphyrin dendrimers **5a**–**c** containing four cationic organoiron moieties (Scheme 2). The relatively weak metal-aryl coordination bonds between the cyclopentadienyliron and the arene ring in the organoiron cation groups can be readily cleaved using UV light at a wavelength of 300 nm in a strongly coordinating solvent such as acetonitrile. Solutions of dendrimers **5a** and **5c** in CH_3CN were exposed to 300 nm light for 2 h to produce metal-free dendrimers **7a** and **5c** (Scheme 2). After cleavage of the cationic cyclopentadienyliron moieties, the solubility of the dendrimers in non-polar organic solvents was found to be drastically increased. The ^{1}H NMR data of dendrimer **7a** shows that the resonance at 5.44 ppm from the cationic cyclopentadienyliron moiety has completely disappeared, confirming the removal of the iron arene moiety.

The reaction of the previously prepared free-base porphyrin and metalloporphyrin dendrimers **3a**–**c** with 4-hydroxybenzyl alcohol (**10**) in the presence of a weak base gave dendrimers that possess terminal primary aliphatic alcohols **4a**–**c** (Scheme 2).

The ^{1}H NMR spectrum of **4b** (Fig. 2) clearly shows the successful incorporation of the 4-hydroxybenzyl alcohol, as evidenced by the presence of the benzyl methylene group doublet at 4.59 ppm. To study the effect of cyclopentadienyliron moieties on the fluorescence and absorption spectra of these compounds, solutions of dendrimer **4a** in CH_3CN were exposed to 300 nm light for 6 h to give the de-metallated dendrimer **4d**, i.e., the corresponding dendrimer without the presence of the cationic cyclopentadienyliron moieties.

The terminal aliphatic alcohol groups of both the free-base porphyrin and the metalloporphyrin dendrimers **4a** and **4c** were esterified using ferrocene carboxylic acid. Carboxylic acid ferrocene is readily synthesized by Friedel–Crafts acetylation, followed by oxidation with iodine. The ease and afforability of its synthesis make carboxylic

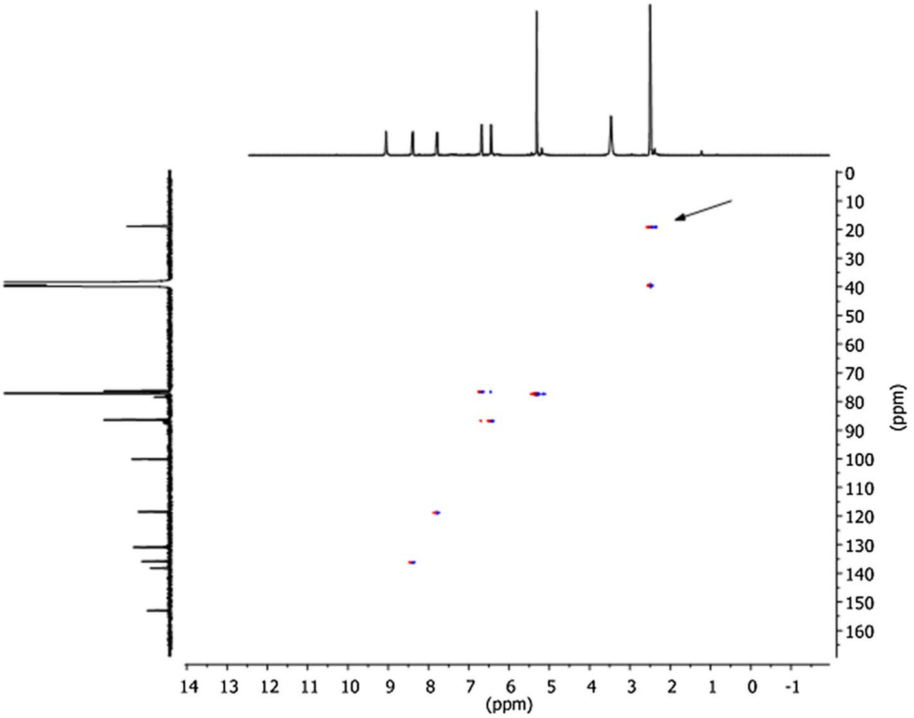
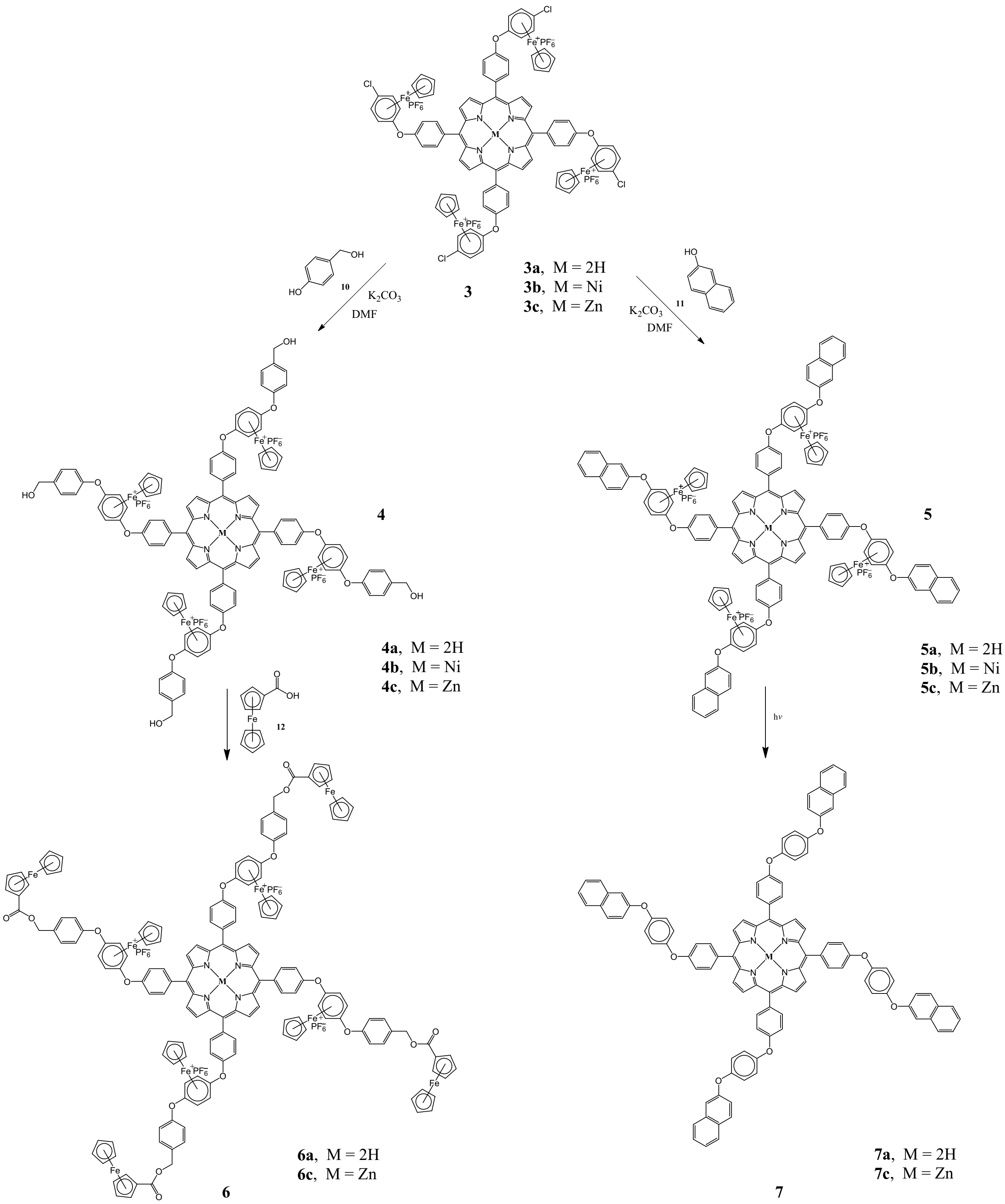


Fig. 1 HSQC spectrum of porphyrin **2a**



Scheme 2 Synthesis of free-base porphyrin and metalloporphyrins 4a–c, 5a–c, 6a, 6c, 7a and 7c

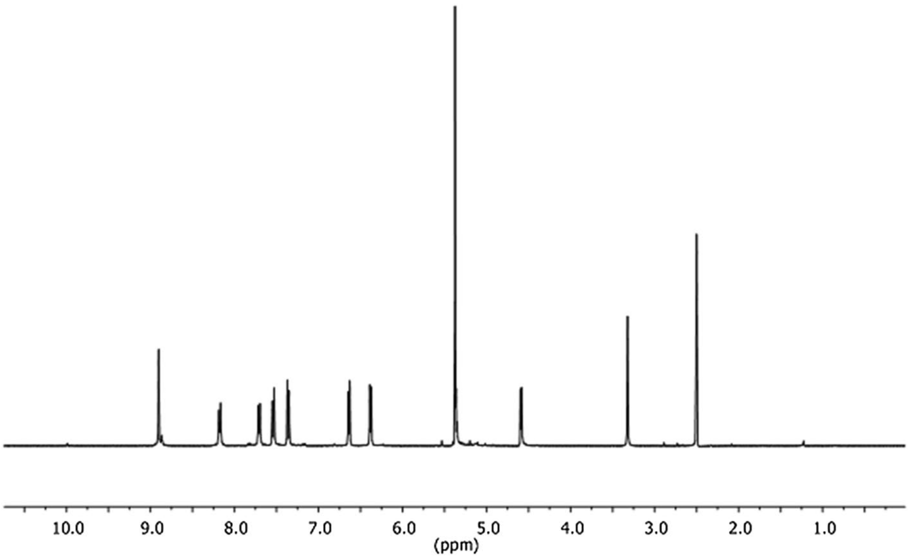


Fig. 2 400 MHz ^{1}H NMR spectrum of metalloporphyrin dendrimer **4b**

acid ferrocene a valuable compound, and its use allows for the incorporation of ferrocene into both free-base porphyrins and metalloporphyrins. The reaction of ferrocene carboxylic acid (**12**) with the terminal aliphatic alcohol groups of free-base porphyrin and metalloporphyrin dendrimers **4a** and **4c** in the presence of DCC/DMAP resulted in the preparation of the ferrocene-capped free-base porphyrin and metalloporphyrin dendrimers **6a** and **6c** (Scheme 2).

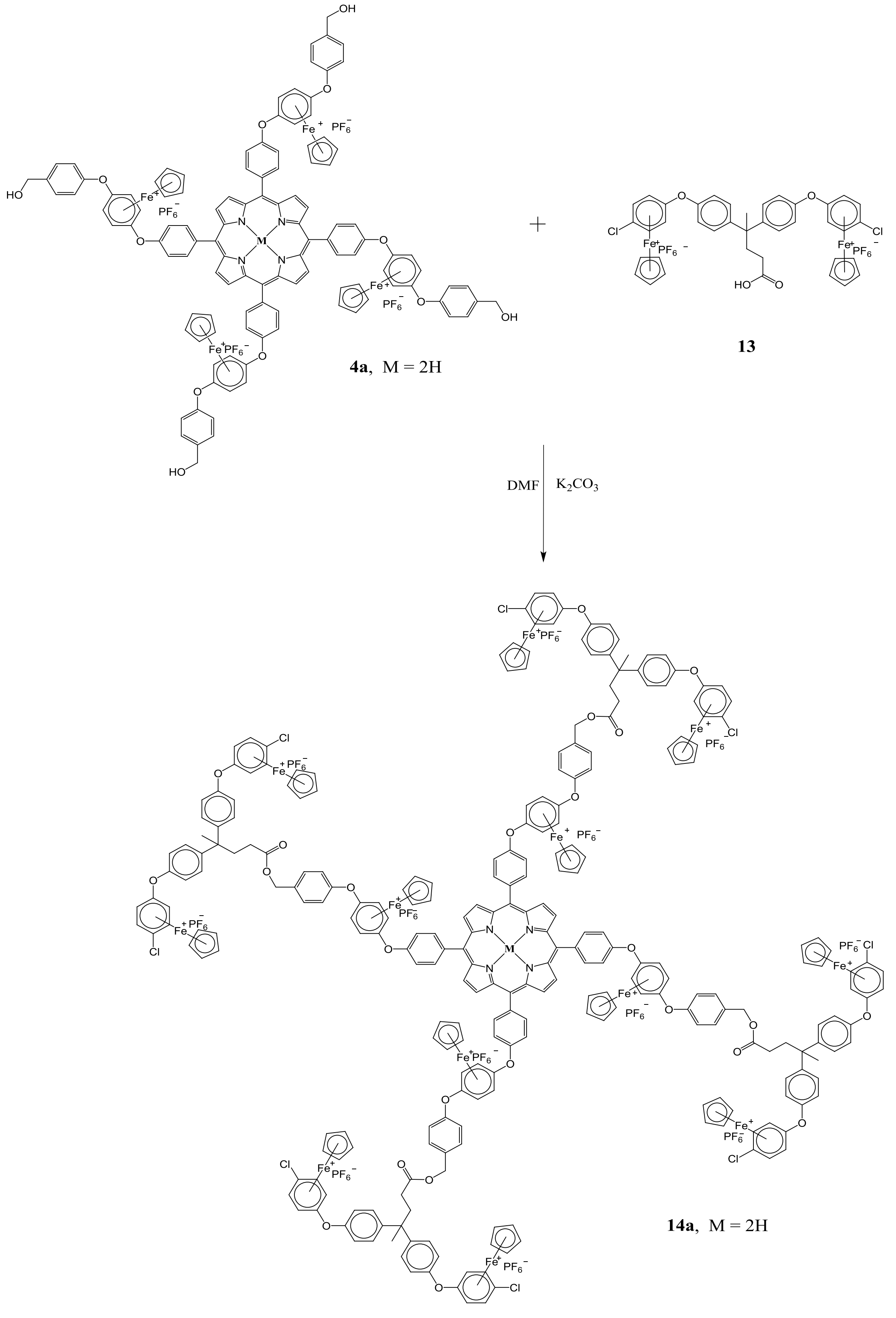
The ^{1}H NMR data confirmed the successful synthesis of the ferrocene-capped porphyrin and metalloporphyrin dendrimers **6a** and **6c**, as indicated by the presence of a new Cp proton resonance at 4.16 ppm arising from non-functionalized Cp ring of ferrocene. There are also two resonances from the functionalized Cp ring at 4.79 ppm and 4.50 ppm. The benzylic CH_2 resonance was also shifted close to the cationic iron Cp at 5.32 ppm due to the increased electron-withdrawing nature of the ester, while the cationic iron Cp resonated at 5.34 ppm. The dendrimers **6a** and **6c** were orange in colour and were highly soluble in organic solvents as a result of the incorporation of the ferrocene moiety into the dendrimer structure.

Additional metallic moieties can be attached to the dendritic porphyrins in order to increase the number of metal species in the molecule. For this purpose, the free-base porphyrin **4a** was reacted with four equivalents of the valeric bimetallic complex (**13**) to yield the free-base porphyrin dendrimer **14a** containing twelve metal centres (Scheme 3). The formation of the second generation of the metallic unit was confirmed by the presence of two different Cp resonances at 5.28 and 5.19 ppm which, when integrated, show a 2:1 ratio, as there are forty and twenty cyclopentadienyliron protons in these two different electronic environments.

3.1 Absorption and Fluorescence Spectroscopy

The absorption spectra obtained for the free-base porphyrin **2a**, Ni-porphyrin complex **2b**, and Zn-porphyrin complex **2c** (Table 1; Fig. 3) showed significant similarity to the absorption spectrum of the corresponding free or metal-complexed porphyrin cores **1a, 1b**, and **1c**. However, a new absorption band appeared at 309 nm, attributed to the incorporation of the cyclopentadienyliron complex onto the porphyrin core. The metal ions in the metalloporphyrins behave as Lewis acids and accept lone pairs of electrons from the dianionic porphyrin ligand. Unlike most transition metal complexes, their color is due to electronic transitions within the porphyrin ligand involving the excitation of electrons from π to π* porphyrin ring orbitals. The change in the spectrum, specifically the fewer peaks in the case of metalloporphyrins, is a result of the increased symmetry of the metallated porphyrin compared to the free-base porphyrin. The two amino hydrogens on present in the free-base porphyrin reduce the ring symmetry from square, in case of metalloporphyrins, to rectangular.

There is significant metal to ligand π-backbonding occurring via the π* orbital of the porphyrin in the Ni-porphyrin complex, which increases the porphyrin π* orbital energy, resulting in an increased porphyrin π–π* energy gap. This causes the electronic absorptions to undergo a slight blue shift relative to the free base porphyrin. In contrast, the Zn-porphyrin complex contains metal d–π orbitals that are relatively low in energy, having very little effect on the porphyrin π–π* energy gap in the electronic spectrum of the porphyrin. As a result, the electronic absorptions of the Zn-porphyrin complex occur at lower energies and therefore the absorption spectrum undergoes red shifts relative to the free base porphyrin.



Scheme 3 Synthesis of free-base porphyrin and metalloporphyrins 14a

Table 1 UV–Visible data of the compounds in DMF (1.5×10^{-5} M)

Compounds	Absorption (λ_{max}/nm)				
	Soret band	Q band			
1a	423	519	557	598	652
1b	418	–	531	–	–
1c	428	–	563	604	–
2a	419	517	553	594	649
2b	415	–	528	–	–
2c	426	–	560	601	–
3a	417	515	550	592	647
3b	414	–	526	–	–
3c	425	–	557	598	–
4a	419	516	552	593	648
4c	426	–	559	600	–
6a	419	516	550	592	649
7a	418	517	551	592	645
7c	426	–	558	597	–
14a	419	516	552	591	647

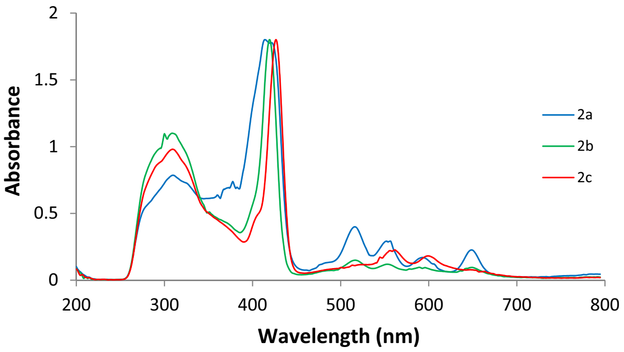


Fig. 3 Absorption spectra of compounds 2a–c in DMF

Table 2 Fluorescence data of the compounds in DMF (1.5×10^{-5} M)

Compounds	Peak fluorescence wavelength (λ_{em}/nm)	
1a	658	716
1c	613	660
2a	653	714
2c	606	655
3a	651	711
3c	604	652
4a	653	716
4c	609	655
6a	653	714
7a	652	713
7c	604	651
14a	653	714

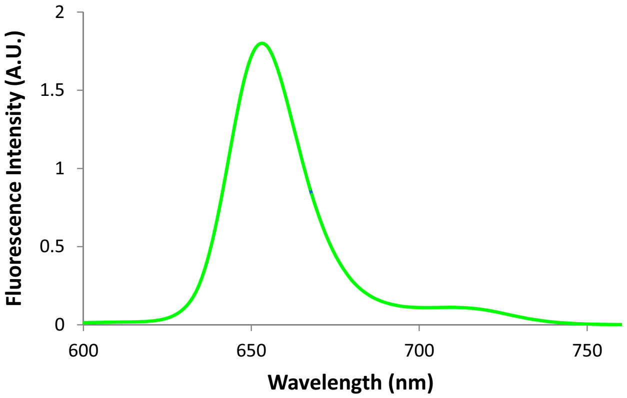


Fig. 4 Fluorescence spectra of free-base porphyrin **2a** excited at 420 nm

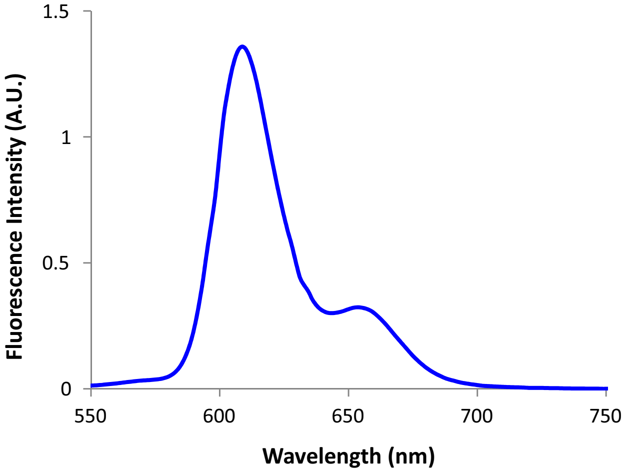


Fig. 5 Fluorescence spectrum of Zn-porphyrin **2c** excited at 420 nm

Fluorescence measurements were performed on both free-base porphyrin **2a** and Zn-porphyrin complex **2c**. All of the fluorescence bands were blue-shifted compared to that of porphyrin cores **1a** and **1c** (Table 2; Figs. 4, 5). The most likely explanation for this observation is that the incorporation of the iron complex decreases the electron density in the porphyrin macrocycle, which raises the energy gap for electronic transition, resulting in a blue shift in the fluorescence bands. More significantly, there is a very large blue shift in the emission band of this dendrimer upon Zn^{2+} complexation, from 653 to 606 nm.

The incorporation of the dichlorobenzene-cyclopentadienyliron moiety **8** into the porphyrin core, which is indicated in the absorption spectrum by bands in the range of 203–268 nm, led to free-base porphyrin **3a** and porphyrin dendrimers containing nickel (**3b**) and zinc (**3c**), all of these exhibiting similar absorption spectra to the corresponding complexes **1a, 1b**, and **1c**. The introduction of electron

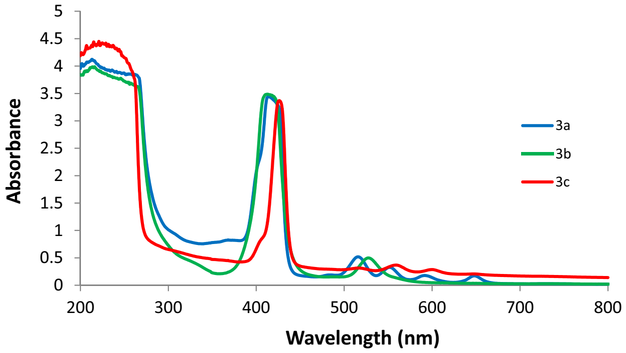


Fig. 6 Absorption spectra of compounds **3a–c** in DMF

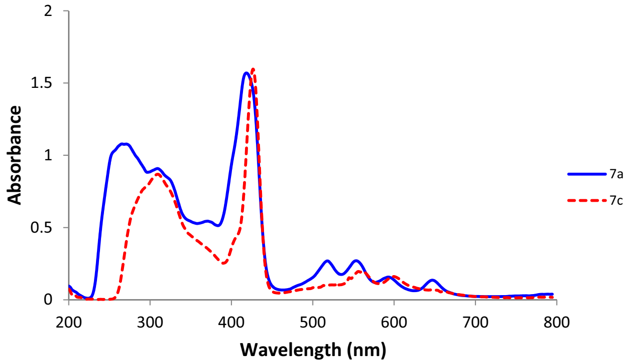


Fig. 8 Absorption spectra of compounds **7a** and **7c** in DMF

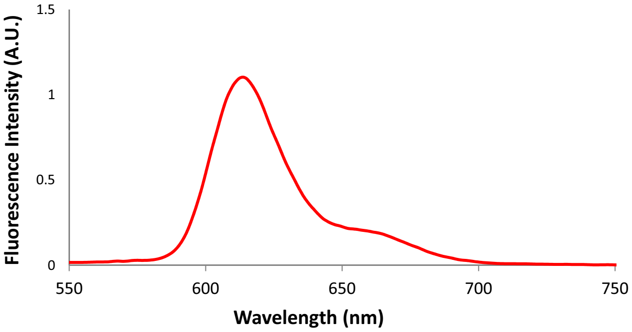


Fig. 7 Fluorescence spectrum of Zn-porphyrin **3c** excited at 420 nm

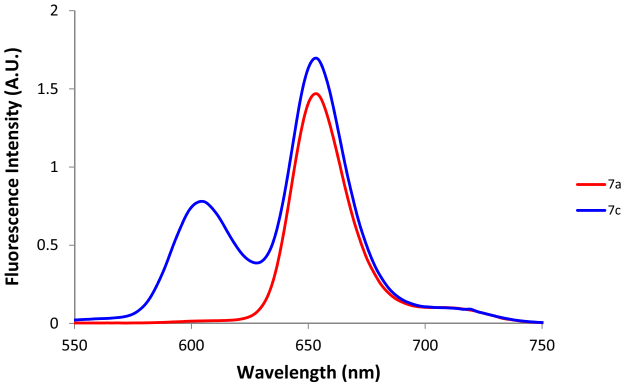


Fig. 9 Fluorescence spectra of free-base porphyrin **7a** and zinc porphyrin dendrimer **7c**

withdrawing groups (complex **9** or **8**) to the *para*-phenyl positions has been shown to lower the energy of the *b1* orbital by decreasing the amount of electron density in this orbital, leading to an increase in the energy of transition and hence blue shifted bands compared to the porphyrin cores (Table 1; Fig. 6). However, the presence of the Cl versus CH_3 substituent had only a minor effect on the emission spectrum, with just a slight blue shift of 2 nm for **3a** and **3c** compared to **2a** and **2c**. Again, there is a very large blue shift in the emission of this compound upon Zn^{2+} complexation, from 651 to 604 nm (Fig. 7).

The incorporation of naphthalene moieties (**11**) into the porphyrin complexes **3a** and **3c** led to free-base porphyrin dendrimer **5a** and Zn-porphyrin dendrimer **5c**. These compounds were also UV-photolyzed in order to cleave the cyclopentadienyliron moiety and produce the corresponding organoiron-free free-base porphyrin dendrimer **7a** and Zn-porphyrin dendrimer **7c**, both with similar absorption spectra to those of **3a** and **3c**, respectively (Table 1; Fig. 8). Thus, the presence or absence of the organoiron moieties has no measurable effect on the fluorescence properties of these compounds, and it is clear therefore that the iron does not quench the porphyrin emission. One difference between **7** and **3** however is the clear presence of the absorption band of naphthalene, in the range of 290–350 nm, which can be clearly seen in Fig. 8. Again, as was seen in the case of compounds **2** and **3**, there is a large blue shift in the emission of this compound upon Zn^{2+} complexation, in this case from 652 nm for compound **7a** to 604 nm in the case of compound **7b**.

The presence of the naphthalene moieties in the case of the free-base dendrimer **7a** and its zinc counterpart **7c** has very little impact on the fluorescence spectrum when the compounds are excited at 420 nm (porphyrin absorption), compared to the spectra of **3a** and **3c**. There is no evidence of naphthalene emission using this porphyrin-based excitation wavelength. Similar to the absorption spectra, the change in the energies of the fluorescence bands was observed for free-base dendrimer **7a**. The free-base dendrimer fluoresced at 652 nm and 713 nm (Table 2; Fig. 9). The Zn-complexed dendrimer **7c** however showed a strong, new band at 610 nm, as shown in Fig. 9, which was not observed in the case of the free base **7a**, or in any of the other compounds for that matter. This is a potentially useful result, as this compound **7c** could find applicability as a metal cation sensor, with the appearance of this strong fluorescence at 610 nm upon

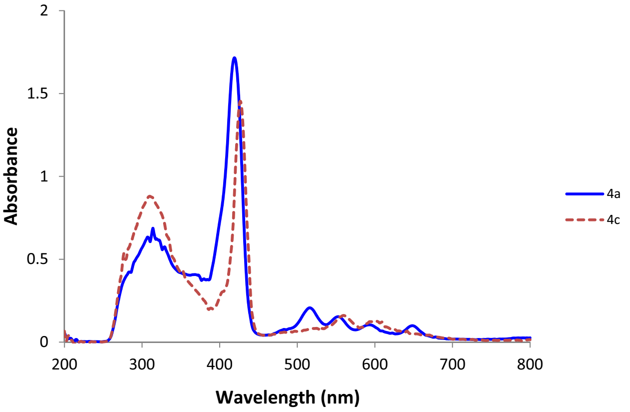


Fig. 10 Absorption spectra of compounds **4a** and **4c** in DMF

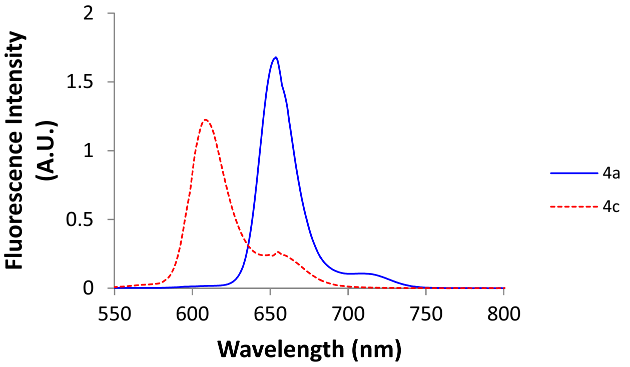


Fig. 11 Fluorescence spectra of compounds **4a** and **4c**

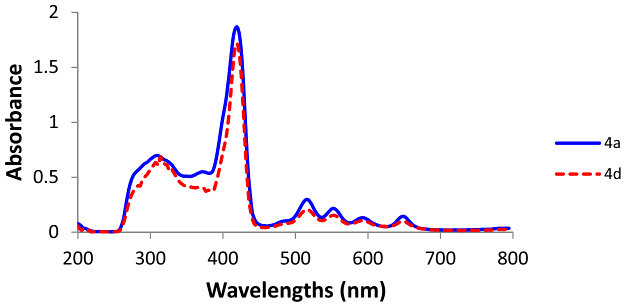


Fig. 12 Absorption of **4a** and demetalated porphyrin **4d** in DMF

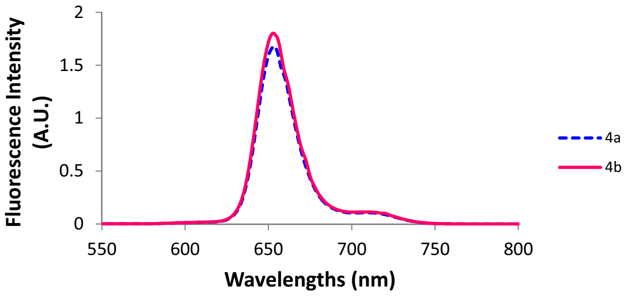


Fig. 13 Fluorescence spectra of porphyrin dendrimers **4a** and **4d**

complexation. This could be achieved by monitoring the fluorescence intensity of a solution of dendrimer **7c**; the intensity of the signal would be correlated to the presence and concentration of Zn^{2+} in the solution. Recent reports of other examples of such metal-cation optical sensors have demonstrated their utility in various applications [37, 38]. Again, as in the case of the previous compounds as described above, there is a very large blue shift in the emission of this compound upon Zn^{2+} complexation, in this case from 652 to 604 nm.

The incorporation of 4-hydroxybenzyl alcohol (**10**) moieties into the previously prepared porphyrin complexes **3a** and **3c** led to the preparation of the free-base porphyrin dendrimer **4a** and its corresponding zinc-based metalloporphyrin dendrimer **4c**, which exhibited slightly red-shifted fluorescence spectra (again, just on the order of 2 nm) compared to those of **3a** and **3c** (Tables 1, 2, Figs. 10, 11). This slight red shift in the absorption and fluorescence bands after the introduction of 4-hydroxybenzyl alcohol moieties can be explained as being a result of the hydroxyl group donating electron density to the aromatic ring, strengthening the resulting electronic density on the phenyl ring. Therefore, the phenyl ring in this case is conjugated with the porphyrin macrocycle, which results in a reduced electron transition energy of the porphyrin macrocycle, resulting in the observed red-shifted peaks in the absorption spectrum. As in the case of the previous compounds, there is a large blue shift in the emission of this compound upon Zn^{2+} complexation, in this specific case from 653 to 609 nm.

To investigate the effect of the cyclopentadienyliron moieties on the fluorescence and absorption spectroscopy of these compounds, the fluorescence and absorption measurements of free-base porphyrin dendrimer **4d** were performed. Interestingly, the fluorescence and absorption spectra were exactly the same as those for the corresponding compound containing the cyclopentadienyliron groups, indicating that the electron transition energy of the porphyrin macrocycle is not measurably affected by the demetallation process (Figs. 12, 13).

Finally, the incorporation of the valeric bimetallic complex **13** and the carboxylic acid ferrocene **12** into the previously prepared porphyrin complex **4a** led to the isolation of free-base porphyrin dendrimers **6a** and **14a**, with no observable shift in the absorption and fluorescence spectra (Tables 1, 2).

4 Conclusions

Novel free-base porphyrins, nickel and zinc porphyrin dendrimers containing cationic η^6-chlorobenzene-η^5-cyclopentadienyliron(II) complexes and cationic η^6-methylbenzene-η^5-cyclopentadienyliron(II) complexes functionalized with naphthalene and capped with ferrocene were synthesized and characterized. The incorporation of cationic η^6-dichloroarene-η^5-cyclopentadienyliron moieties into these dendrimeric structures enhanced the solubility of the dendrimer and facilitated further nucleophilic aromatic substitution and addition reactions, as a result of the strong electron-withdrawing ability of the iron center. However, the results found here show that the presence of the organoiron groups has no significant effect on the fluorescence properties of these compounds, and it is concluded that the iron cations do not quench the porphyrin emission. This is important for the potential application of these compounds as fluorescent sensors. Divergent approaches were also employed to give highly symmetrical branched materials.

Photophysical studies of these dendrimers showed that the incorporation of various terminal methyl group cyclopentadienyliron complexes led to a small blue shift in the absorption spectra on the order of ~ 3 nm, while the incorporation of the terminal chloro group cyclopentadienyliron complex led to a slightly larger blue shift in the absorption spectra on the order of ~ 6 nm. This shift is most likely due to the incorporation of the iron complexes decreasing the electron density in the porphyrin macrocycle, which thereby raised the energy of electron transition, leading to a blue shift in the absorption and fluorescence spectra. On the other hand, the presence of the electron-donating group, naphthalene, resulted in no significant shift of either the absorption or fluorescence spectrum (≤ 1 nm), indicating the negligible impact of the naphthalene moiety on the electronic properties of the porphyrin macrocycle.

In all cases, addition of various chains and terminal groups to the porphyrin core did not significantly change the overall fluorescence properties of these series of compounds, with only slight spectral shifts on the order of 6 nm or less, as described above. In fact, in the case of the wide range of porphyrin dendrimers synthesized and characterized, the emission maximum of the free base form was found to be in the range of 651–653 nm in all cases. This opens up the synthetic possibilities for these types of compounds, allowing for the synthesis of a wide range of porphyrin-core dendrimers which retain the desired fluorescence properties. Most importantly, all of these compounds showed a significantly large blue shift of the emission (on the order of close to 50 nm!) upon complexation of Zn^{2+} cations, opening up the possibility of the utilization of these compounds as optical sensors for metal cations.

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